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COMMONWEALTH OF PENNSYLVANIA

DEPARTMENT OF INTERNAL AFFAIRS

THE OCCURRENCE OF BRINE IN WESTERN PENNSYLVANIA

by

Charles W. Poth

TOPOGRAPHIC AND GEOLOGIC SURVEY

BULLETIN M 47

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THE OCCURRENCE OF BRINE IN WESTERN PENNSYLVANIA

by

Charles W. Poth
U. S. Geological Survey

Prepared by
The United States Geological Survey
Ground Water Branch
in cooperation with
The Pennsylvania Geological Survey

DEPARTMENT OF INTERNAL AFFAIRS
Genevieve Blatt, Secretary
TOPOGRAPHIC AND GEOLOGIC SURVEY
Arthur A. Socolow, State Geologist
1962

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THE OCCURRENCE OF BRINE IN WESTERN PENNSYLVANIA

By Charles W. Poth

ABSTRACT

Fifty-one samples of brine were collected from 14 formations that range in age from Cambrian to Pennsylvanian. Complete chemical analyses were made of 37 samples and partial analyses were made of 14 others. Iron, manganese, strontium, and barium were determined spectrographically in 28 samples and lithium, rubidium, and cesium in 3.

The major constituents (present in amounts greater than 1,000 ppm) consist of chloride, sodium, calcium, and magnesium; the minor ones (only rarely exceeding 1,000 ppm) include bromide, potassium, strontium, and barium. The concentrations of major and minor constituents, except barium, are shown to have high correlation with the dissolved-solids content. The relation is linear and equations are given for calculating the concentration of these elements from the dissolved-solids content. Ion exchange causes deviation from the linear relationship at higher concentrations (above 140,000 ppm) of dissolved solids. The concentrations of trace constituents—silica, iron, aluminum, manganese, copper, zinc, lithium, iodide, and fluoride—are not closely related to the dissolved solids content, and rarely exceed 100 ppm. The dissolved-solids content is commonly as great as 100,000 ppm and in the deeper formations may exceed 300,000 ppm. Thus, the brine compares favorably in concentration with brine from other areas.

The brine is considered to have formed by the mechanism suggested by DeSitter (1947): first, part of the alkaline earths are removed, and then, the brine is concentrated by squeezing out part of the water. The lower sodium-calcium ratio in very concentrated brine, however, is ascribed to ion exchange rather than to DeSitter's differential enrichment from pellicular water.

INTRODUCTION

PURPOSE AND SCOPE

The purpose of this report is to summarize the occurrence and chemical quality of brine in western Pennsylvania. Fifty-one brine samples were collected by members of the Pennsylvania Geological Survey and analyzed by the U. S. Geological Survey. Available literature on the geology of western Pennsylvania was studied in order to present a coordinated summary of the geologic section in the area.

Brine is a byproduct of most oil and gas production. In some areas brine has been considered a troublesome waste material to be disposed of as inexpensively as possible. The methods of disposal differ—depending on the operator and local regulations—but consist, usually, either of pumping the brine out upon the ground, to evaporation ponds, or down a wall. The evaporation ponds commonly are ineffective because the water seeps rapidly into the ground through their leaky bottoms. They are a source of contamination to surface streams and to shallow, fresh-water aquifers.

Returning the waste water to a formation lying below the fresh-water bearing beds, via a well, is an expensive procedure which the operator understandably is reluctant to employ except where he can use the water for hydraulic drive in the secondary recovery of oil.

Since colonial times there has been an interest in the brines. Salt springs and brine wells served as the chief source of salt to the pioneers in some areas. It is interesting to note that the drillers hired by Colonel Drake to drill the first successful oil well had learned their trade in the brine industry (Lytle, 1959, p. 14).

Today brine is processed in some states not only for its major salts—the chlorides of sodium, calcium, and magnesium—but also for such minor constituents as bromide and iodide. Chlorine, caustic soda, and hydrogen are obtained through electrolysis of the brine.

In western Pennsylvania brine is of interest for two reasons: (1) it is a possible contaminant of fresh water, and (2) it is a potentially important natural resource, the development of which might aid in the industrialization and economic stability of the areas in which it occurs. For these reasons a reconnaissance study of the occurrence and chemical character of oil- and gas-field waters was undertaken with the cooperation of the Regional Industrial Development Corp., a nonprofit organization dedicated to the industrial development of the Pittsburgh region, and the Pennsylvania Topographic and Geologic Survey.

Location of Area

The area from which samples were collected in this investigation includes Allegheny, Beaver, Butler, Clearfield, Erie, Lawrence, Washington, and Westmoreland Counties in the Appalachian Plateau Province of western Pennsylvania. (See Fig. 1.) The location of the wells sampled is given in Figure 2.

Methods of this Investigation

Sampling

Brine samples were taken to obtain information over as wide an area and geologic range as possible. An effort was also made to acquire some understanding of the variation in the brine within a single formation. There was, however, no free choice in the selection of sample sites. Drilling activity in the Plateau region was not sufficient to allow the sampling of new wells only, so both new and old wells were sampled. As most of the old wells were pumped at irregular intervals, it was necessary for the collector to cruise the area of interest until he found a well being pumped. He then obtained geologic information on the well from the operator, and if the well appeared to be a satisfactory sampling site he collected a sample of water. Records of the wells sampled are given in Appendix I.

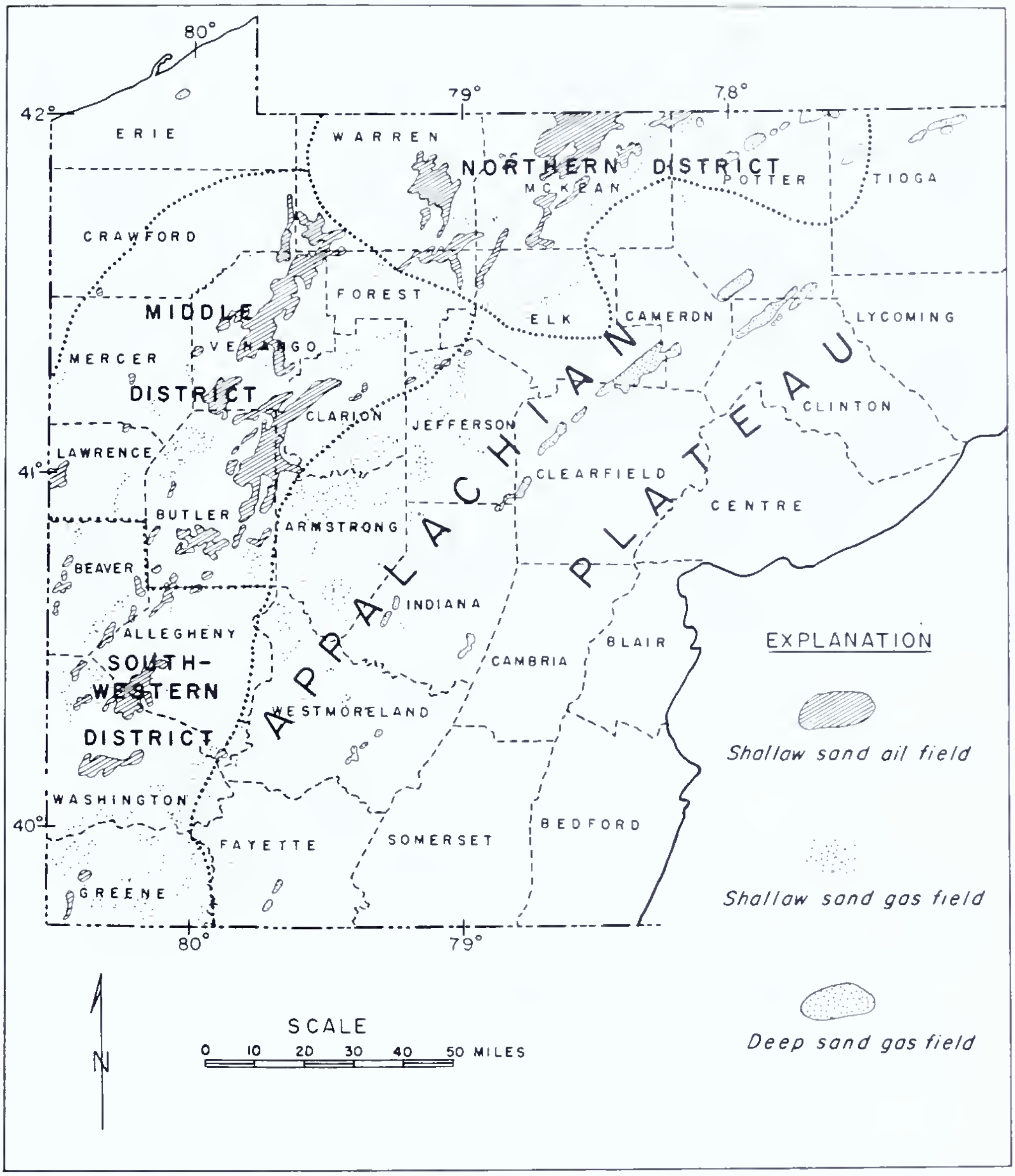


Figure 1. **Map showing location of shallow oil and shallow and deep gas fields and boundaries of northern, middle, and southwestern districts. (After Lytle and others, 1959).**

Chemical analytical techniques

Of the fifty-one brine samples collected and filtered in the field to remove rust and other foreign particles, 35 were analyzed by the U. S. Geological Survey in Washington, D. C. using both wet-chemical and spectrographic methods. The remaining 16 samples were analyzed by wet-chemical methods by U. S. Geological Survey in Philadelphia, Pa. The analytical results are given in Appendixes 2 and 3.

Standard methods (Rainwater and Thatcher, 1960) were employed in the wet-chemical analyses, and because little work has been done spectrographically on brines, several techniques were tried in the spectrographic determinations. The samples were first analyzed by direct-spark determinations on the water. Sodium, calcium, and magnesium were detected as major constituents and strontium and barium as minor constituents. In the next techniques employed, the samples were evaporated to dryness, and the residues were dried at 180° C. and analyzed in a direct current arc (Haffty, 1960). By the latter technique, traces of silicon, iron, manganese, aluminum, silver, boron, chromium, and copper were detected in addition to those elements first mentioned. The last seven samples were arced in the visible and near-infrared range also, to determine lithium, cesium, and rubidium. Only strontium, barium, manganese, iron, and lithium were determined quantitatively.

The chemical and spectrographic methods for determining manganese, iron, and strontium were compared statistically by means of "Student's" t-test, using the formula:

$$t = \frac{\frac{\Sigma X_1}{N} - \frac{\Sigma X_2}{N}}{\sqrt{\frac{\Sigma(X_1 - X_2)^2 - \frac{(\Sigma X_1 - \Sigma X_2)^2}{N}}{N(N-1)}}}$$

where

X_1 is a value obtained by the first method,

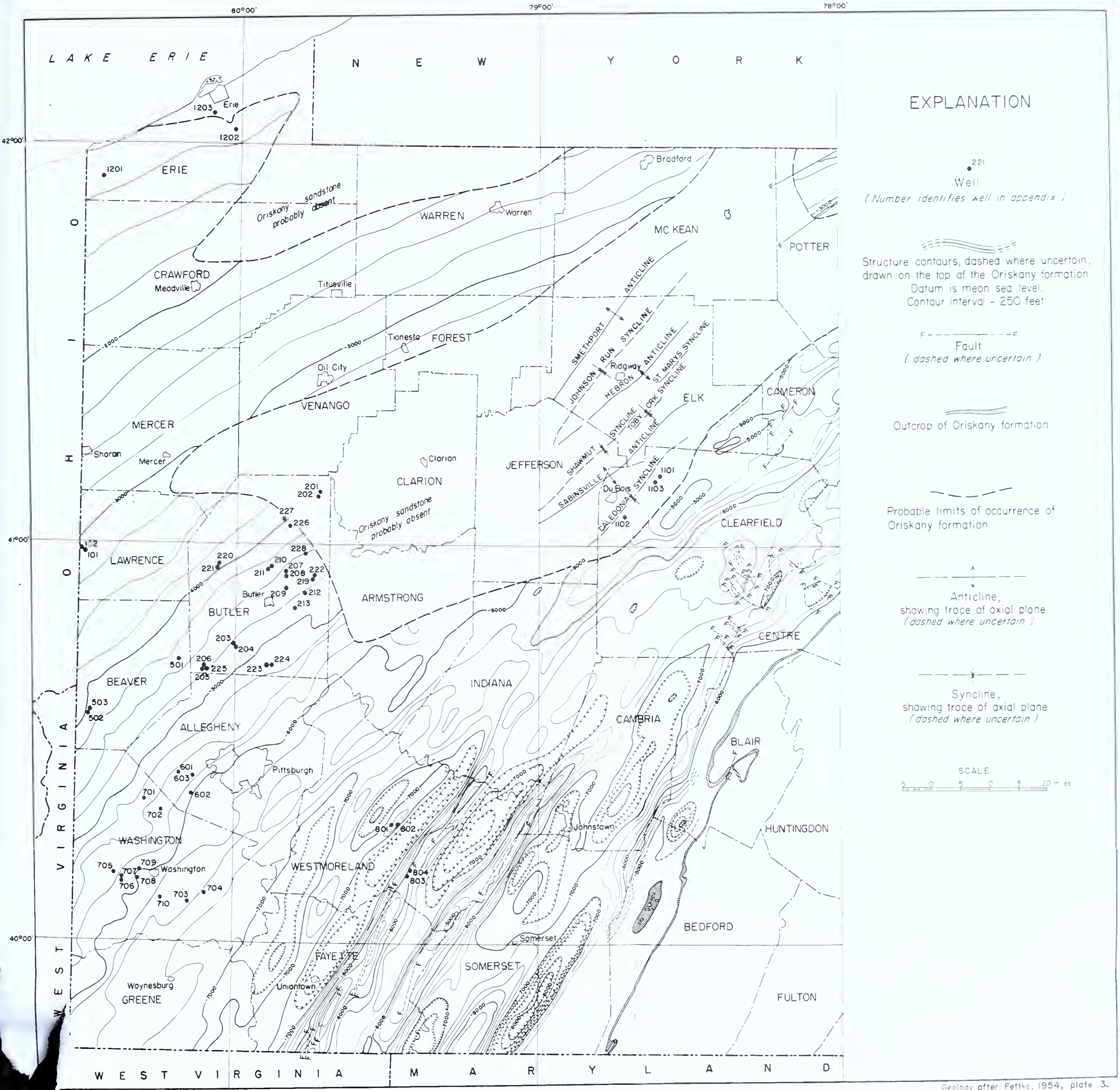
X_2 is a value obtained by the second method

N is the number of pairs of samples.

Colorimetry was employed for the chemical determination of the first two elements and flame photometry for strontium.

It has been shown that any statistic divided by the standard deviation of its mean is distributed in a t-distribution. First described by W. S. Gossett (Student) in 1908, this distribution has proved invaluable in the comparison of populations represented only by small samples. The precision of the test is greatly increased by the use of paired samples wherever the conditions are suitable. Paired samples have been used for this study and the results are summarized in Table 1.

The theoretical "t" for the different numbers of degrees of freedom of the difference elements (one less than the number of pairs of samples) for several probabilities is given in the table for convenient reference. The table is interpreted as follows: If no differences exist between the methods of analysis, the calculated "t" will be small, as in the case of manganese. If the calculated "t" is equal to or greater than the theoretical "$t_{.05}$", the probability of obtaining so large a value through chance alone is about 5 in



se from U.S. Geological Survey base map of Pennsylvania, 1927

Geology after Fettke, 1954, plate 3.
Well locations by Poth, 1959.

Figure 2. Map showing well locations and subsurface structure contours on the top of the Oriskany formation in western Pennsylvania.

Table 1. *Comparison of chemical and spectrographic methods for manganese, iron, and strontium by means of Student's t-test, using paired samples.*

			Theoretical		
Element	No. of pairs of samples	Calculated "t"	t .05	t .025	t .0125
Manganese	27	0.204	1.70	2.05	2.37
Iron	28	2.11	1.70	2.05	2.37
Strontium	14	2.29	1.77	2.16	2.53

100. The experimenter must decide on the chances he wishes to take in accepting or rejecting an hypothesis, but it is generally customary to consider as suspect an event which may be expected to occur only about 5 percent of the time and to reject it at a 1 percent probability.

Remarkably close agreement was found to exist between determinations made for manganese by the chemical and spectrographic methods; however, the results of the two methods differed significantly in the case of both iron and strontium. Spectrographically determined iron concentrations were higher than those determined chemically, and the reverse was true for strontium.

GEOLOGY OF THE PLATEAU SEDIMENTS[1]

The geology of the sediments of the Appalachian Plateau is presented here in some detail in order to provide an adequate basis for this summary and for future investigations of the brines of Pennsylvania.

Oil and gas wells in Pennsylvania have penetrated formations ranging in age from Precambrian to Permian. Wells producing from Upper Devonian or younger beds are commonly referred to as "shallow" wells (Lytle and others, 1959, p. 1), and those penetrating older (and, hence, generally deeper) beds are termed "deep" wells. A general geologic section for north-central and western Pennsylvania is shown on Table 2. The distribution of shallow and deep fields is shown in Figure 1.

Exploration of the older formations has increased considerably since 1930. Although prior to 1930 only 36 "deep" wells had been drilled, by the end of 1958 the number had reached 1,860, of which 1,044 were gas wells, 2 yielded oil and gas, 744 were "dry" (that is, barren of both oil and gas though not necessarily of water), and 70 were drilled for gas storage (Lytle and others, 1959, p. 4).

---

[1] The geologic names used in the following stratigraphic discussion are those of Fettke (1950) and Lytle (1959) and do not necessarily agree with the usage of the U. S. Geological Survey or the Pennsylvania Topographic and Geologic Survey.

Table 2. *General geologic section for north-central and western Pennsylvania (after Fettke, 1950).*

System	Series	Group or Formation	Description	Approximate thickness in feet
Permian	Dunkard	Greene	Predominately shale, in part red, sandy shale, and shaly sandstone; a few massive sandstones; several thin coal and fresh-water limestone beds.	1,100
		Washington	Shales, sandstones, and thin beds of coal and fresh-water limestone	
Pennsylvanian		Monongahela	Shale, and fresh-water limestone, subordinate sandstone, several workable coal beds.	330
		Conemaugh	Shale, in part.red, and subordinate sandstone; several thin coal and fresh-water and marine limestone beds.	600
		Allegheny	Shale and subordinate sandstone and limestone; several workable coal and fire clay beds.	175
		Pottsville	Massive medium- to coarse-grained sandstone and subordinate shale, clay and limestone.	315
Unconformity			An erosional unconformity bevels sucessively younger southerly dipping Mississippian strata in going from north to south in western Pennsylvania	
Mississippian		Mauch Chunk	Gray and red shale, subordinate fine-grained sandstone.	0 – 100
		Pocono	Fine to coarse-grained massive sandstone and shale.	570 – 900
Devonian	Upper Devonian	Conewango	Gray shale and subordinate fine- to coarse-grained light-gray sandstone; red shale prominent in lower part in northern district; some purplish-red shale in middle and southwestern districts.	3,300 to 6,000 from northwest to southeast
		Conneaut	Gray and purplish-gray shale and sandy shale, subordinate sandstone.	
		Canadaway	Gray shale and sandy shale, subordinate fine- to coarse-grained light gray sandstone and fine-grained chocolate-brown sandstone.	
		Chemung	Gray shale and sandy shale, subordinate fine-grained sandstone.	
		Portage	Gray shale and sandy shale	

	Middle Devonian	Tully	Argillaceous limestone	0 – 150
		Hamilton	Dark gray and black shale, in part calcareous	140 – 1,600
		Onondaga	Cherty limestone and chert, subordinate dark, silty, shaly and glauconitic beds.	30 – 290
	Lower Devonian	Oriskany	Medium-grained quartz sandstone, locally calcareous. Source of gas in north-central and in southwestern Pennsylvania.	0 – 110
		Helderberg	Non-magnesium, in part cherty, frequently very fossiliferous limestone.	0 – 350
Silurian	Upper Silurian or Cayugan	Cobleskill	Argillaceous magnesium limestone	25 – 100
		Salina	Interbedded, dense, argillaceous, magnesium limestone, gray shales and clays for the most part either calcareous or dolomitic. Numerous interbedded layers of anhydrite and salt.	450 – 2,800
	Middle Silurian or Niagaran	Lockport	Very fine, crystalline, brownish-gray to very dark grayish brown relatively pure dolomite. A salt-water zone frequently present.	240 – 320
		Clinton	Shale, dolomitic shale, and subordinate dolomite.	100 – 300
	Lower Silurian or Albion	Thorold	Fine-grained, light-gray sandstone	0 – 30
		Grimsby or Red Medina	Red sandstone and shale. Small gas production in northwestern Pennsylvania	70 – 220
		Cabot Head or Manitoulin	Gray shale and subordinate very fine-grained light-gray sandstone	
		Whirlpool or White Medina	Fine-grained light-gray sandstone. Small gas production in northwestern Pennsylvania	

Table 2. *(concluded)*

Ordovician	Upper Ordovician or Cincinnatian	Queenston	Red shale, in part silty and sandy	850 – 1,200
		Oswego	Very fine-grained gray sandstone	0 – 60
		Reedsville	Gray shale	700 – 800
		Utica	Black shale	100 – 300
	Middle Ordovician or Champlainian	Trenton and Black River	Limestone, in part argillaceous, and either non-magnesium or only slightly magnesium	650 – 750
	Unconformity		Approximately 4,500 feet of Lower Ordovician strata present in central Pennsylvania are missing in western Pennsylvania	
	Lower Ordovician or Canadian	Lower Beekmantown	Fine- to medium, crystalline, light-gray dolomite	0 – 190
Cambrian	Upper Cambrian	Gatesburg	Fine, crystalline, light brownish-gray dolomite with siliceous-oolite zone near middle. Grades into fine, crystalline, sandy dolomite and fine- to medium-grained, light-gray, somewhat dolomitic sandstone in lower part	350+

Although more than 200,000 shallow wells have been drilled in the State of Pennsylvania (W. S. Lytle, 1959, personal communication), geologic information is not available for most of these wells. Partial logs, showing depth to the "pay" horizon and possibly noting the tops of a few prominent shallower beds, are available for a few wells, and cores are available for a few others. Despite the scarcity of detailed subsurface information, the general aspects of the subsurface geology of western Pennsylvania are known.

STRATIGRAPHY

Precambrian rocks

The first test well in western Pennsylvania to reach Precambrian rocks was drilled in Crawford County in 1958 to a depth of 8,030 feet (Lytle and others, 1959, p. 4). No log was released and the well was abandoned.

Cambrian system

Ten wells have penetrated as deep as the Gatesburg formation of Late Cambrian age. The formation is at least 350 feet thick and consists of dolomite, sandy dolomite, and dolomitic sandstone. Available information is insufficient to permit a satisfactory description of the stratigraphy, areal extent, or brine potential of the beds.

Ordovician system

Deposition of carbonate rocks continued into Ordovician time throughout the area as the Beekmantown dolomite was laid down. It ranges in thickness in western Pennsylvania from zero to 190 feet. In the central part of the State the Lower Ordovician is represented by about 4,500 feet of rock (Fettke, 1950a, p. 10). This marked disparity of thickness of the strata between the two areas, plus a distinct change in the fossil content in the overlying formations in the western part of the state constitutes local evidence of a major unconformity.

During the Middle Ordovician 650 to 750 feet of limestone of the Trenton and Black River formations were deposited.

Upper Ordovician (Cincinnatian) sedimentation began with the deposition of 100 to 300 feet of black Utica shale, grading upward into the gray Reedsville shale, which is 700 to 800 feet thick. At this time a large delta, known as the Queenston delta, spread westward across the New York-Pennsylvania region. Deposition in western Pennsylvania became coarser, resulting, in places, in the deposition of as much as 60 feet of the gray, very fine-grained Oswego sandstone. The Ordovician period closed in western

Pennsylvania after deposition of red beds, constituting the Queenston shale, which is 850 to 1,200 feet thick.

Silurian system

Following the climax of the Taconic orogeny at the close of the Ordovician, shallow seas spread across Pennsylvania again, submerging the western part of the delta and depositing the gray, fine-grained Whirlpool sandstone which grades upward and westward into the Cabot Head shale. The Queenston delta continued to grow westward and red beds (Grimsby sandstone) were deposited again in the area for a short time. Then the seas advanced eastward once more and deposited the Thorold sandstone. The present-day occurrence of gas pools in the Albion series marks the approximate positions of the shoreline during Early Silurian time (Fettke, 1940).

Large production of gas from the Albion in adjoining states has spurred the exploration of these beds in the Plateau region of Pennsylvania. As a result, as much as 250 feet of clastic rocks is known to be present.

During Middle Silurian time, deposition of clastic sediments decreased as the land was worn down. The Clinton formation became increasingly dolomitic upward and was succeeded by the Lockport dolomite. The former thickens eastward from 100 to 300 feet; however, as the Lockport received only negligible amounts of sediment from the eastern landmass, it has a relatively uniform thickness of about 270 feet.

Intercalated beds of carbonate rocks, clay, anhydrite, and salt of the Salina formation characterize the Upper Silurian and locally reach combined thicknesses as great as 2,800 feet. The great thickness and repeated occurrence of the anhydrite and salt beds offer convincing evidence of the intensive and sustained aridity of Late Silurian time. Toward the end of the period a return to a marine environment occurred as the Cobleskill limestone was deposited.

Devonian system

Quiescence marked the transition from Silurian to Devonian time throughout eastern North America. The deposition of limestone continued in Pennsylvania; about 350 feet of Helderberg limestone was laid down. The magnesian content of the Helderberg is less than that of the Cobleskill and parts are cherty.

The Oriskany formation, which overlies the Helderberg, is of great areal extent. It is a coarse grained sandstone, nearly free of clay, and is thought to have been formed by the reworking of a highly weathered arenaceous mantle rather than by the erosion of a newly uplifted highland. Its great purity has made it one of the principal sources of glass sand. The Oriskany is absent from a small area in northwestern Pennsylvania because of either nondeposition or pre-Onondaga erosion. Its thickness ranges from zero in northwestern Pennsylvania to as much as 110 feet in Washington and Fayette Counties in the southwestern part of the State, where the Oriskany changes in character to a sandy limestone.

Overlying these Lower Devonian sediments is the cherty Onondaga limestone of Middle Devonian age, which has a maximum thickness of nearly 300 feet. Black and dark-gray shales of the Hamilton shale overlie the Onondaga and in places are as much as 1,600 feet thick.

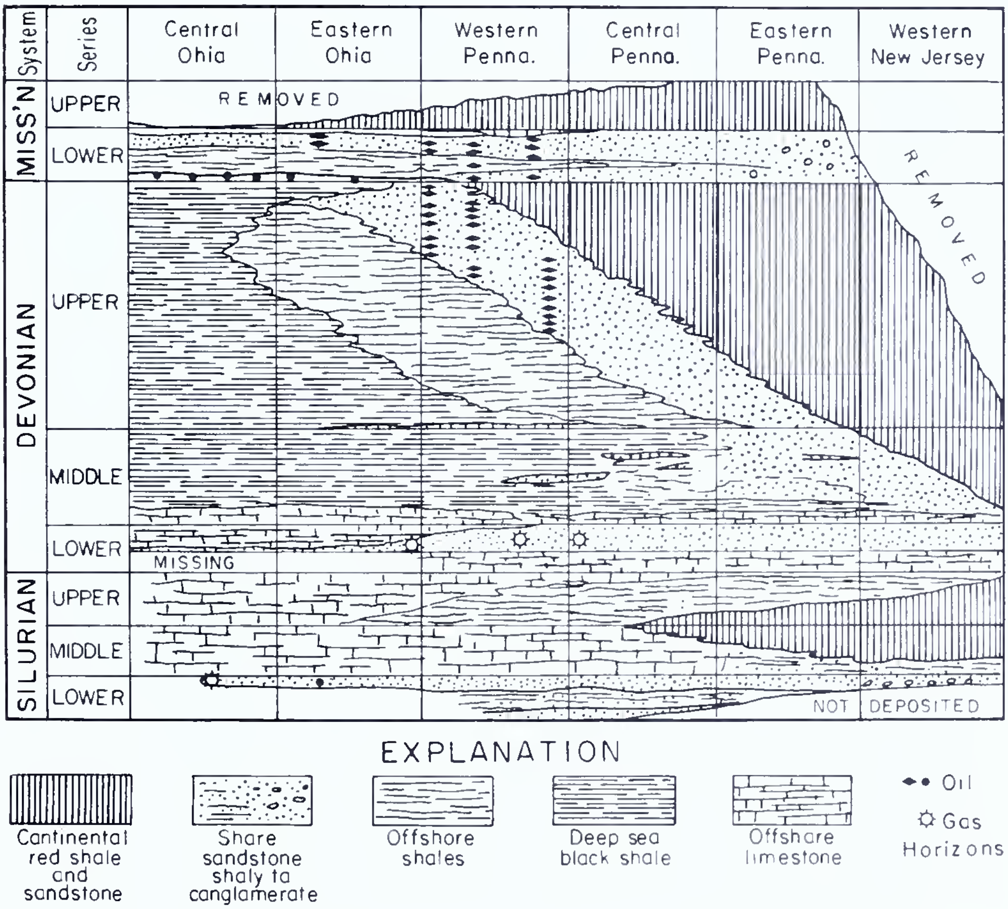


Figure 3. Chart showing changing rock facies from east to west between New Jersey and Ohio. (After Ashley, 1938).

The youngest of the Middle Devonian formations and the uppermost of the "deep sands" is the Tully limestone. It exceeds 200 feet in thickness along its outcrop in Clinton and Lycoming Counties (Willard, cited in Fettke, 1940), and has proved to be an excellent horizon marker throughout a large part of the Plateau.

Upper Devonian sediments overlying the Tully comprise a vast sequence of interfingering marine sandstone and shale that is divided into the following six groups, from oldest to youngest: Genesee, Portage, Chemung, Canadaway, Conneaut, and Conewango. According to Fettke (1950a, p. 9), their thickness increases from 3,300 feet in the northwestern part of the plateau to as much as 6,000 feet in the southeastern part. Formations of the Chemung group, which crop out along the Allegheny Front and in the extreme northwestern part of the State, are the oldest sediments exposed in the Allegheny Plateau. The beds thin northwestward because of the increased distance from the source of the sediments, and because of erosion which is continuing today.

During late Middle Devonian time a great delta began to grow westward across the State. Initially the rising landmass to the east was evidenced in Pennsylvania only by the introduction of clay in the Tully limestone. However, as the volume of sediment increased, fine-grained dark shales were deposited. These in turn gave way to sandy shales and thin-bedded sandstones, and as the delta continued to encroach upon the shallow seaway, gray marine sandstones and shales were gradually replaced by the red and green continental deposits of the Catskill delta. Thus the sediments reflect a shoreline which migrated steadily westward, with minor and only temporary reversals. Figure 3 illustrates the succession of facies in the Appalachian basin during Silurian through Mississippian time.

The first of the "oil sands" began to accumulate during the Canadaway time (Fig. 4). These "sands" are usually of small areal extent and, with few exceptions, have been recognized only in the subsurface. Therefore, most of these shallow beds are known only by local informal names. In the northern district these include the Lower and Upper Kane, Bradford Third, Cooper, Bradford Second, Tiona, Cherry Grove, Balltown, Clarendon, and several others. The Lower and Upper Kane, Bradford Third, Speechley, and several other sands were laid down at this time in the middle district; as was the Speechley sand of the southwestern district. The "oil sands" of the Canadaway group range in color from light gray to chocolate brown. The approximate boundaries of these districts are shown in Figure 1 and the correlation of the sands between districts is shown in Figure 4.

The Conneaut group includes chiefly the Bradford First and Warren sands in the northern and middle districts and the Elizabeth and Bayard sands in the McDonald area. Their colors range from gray to purplish gray. A large part of the group is made up of "pink rocks" (Fig. 4), suggesting a continental or near-continental environment of deposition.

The important petroliferous Knox and Venango sands were deposited during Conewango time in the northern and middle districts, as were the McDonald, Gordon, and Ninevah sands in the southwestern district. The predominant color is gray, though red shale is present in significant amounts in the lower part of the Conewango in the northern district and purplish red shales occur elsewhere in the sequence.

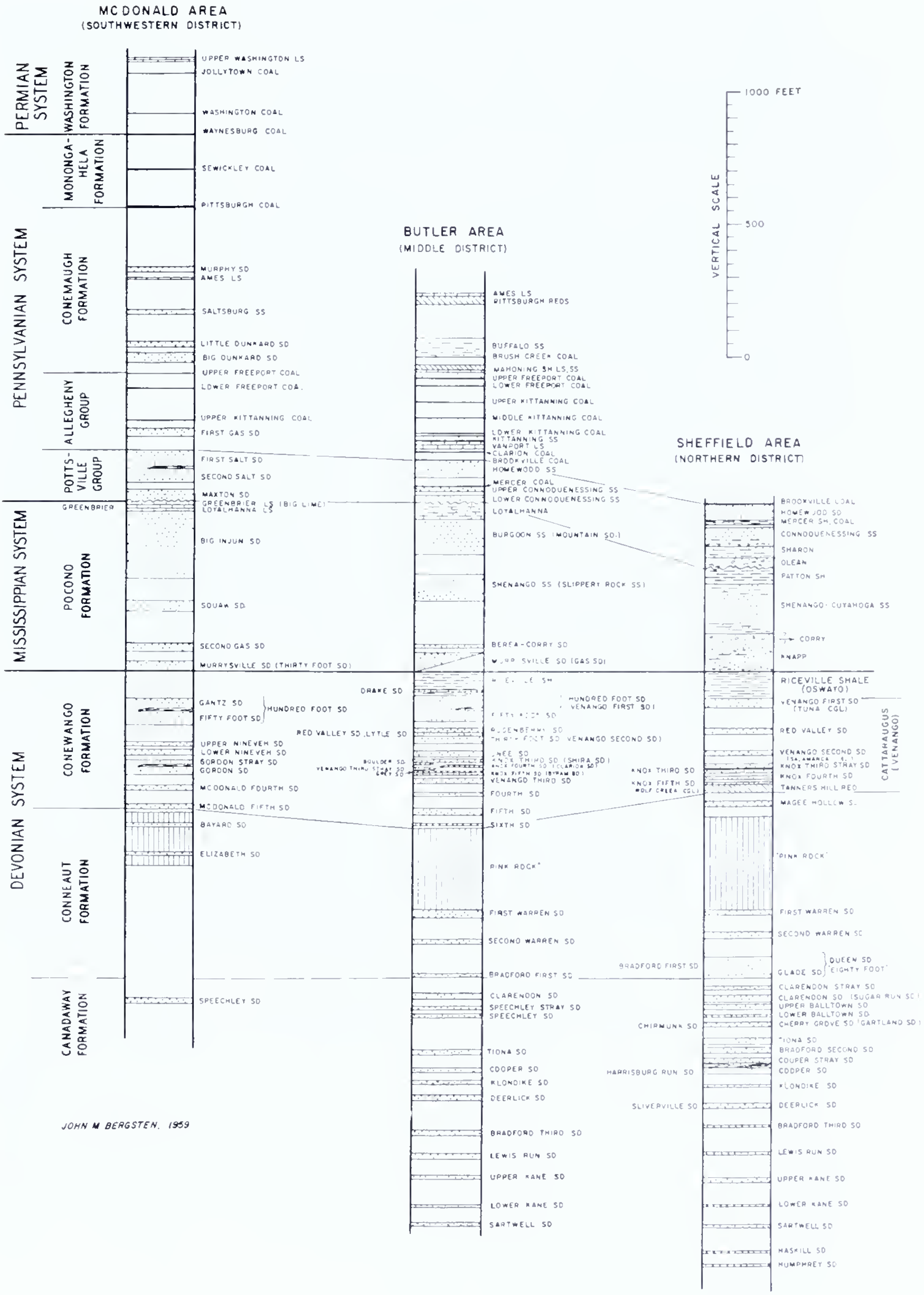


Figure 4. Columnar sections showing stratigraphic positions of oil and gas sands of western Pennsylvania.

The Conewango group is composed principally of shale and sandy shale interbedded with irregular, discontinuous bodies of sandstone. In cross section the beds of sandstone are seen to be plano-convex lenses having the convex side upward. The lenses may unite with others along the strike or grade laterally into shale. Within a district, at least, they do not appear to join with sand bodies of another formation. The shale sequences, on the other hand, are laterally extensive. Marine fossils may be found, especially toward the northwest margins of the sandstone lenses and in the shales.

These marine sandstone lenses are generally narrow and trend northeastward. Northwestward they grade over short distances into marine shale and southeastward they grade over short distances through sandy shale into continental beds. The grain size ranges from very fine sand to cobbles several inches across. Although the coarse fractions may occur anywhere from top to bottom, they are more abundant near and at the top of the lenses and are commonly concentrated on the northwest side.

The Venango sands are composed predominantly of quartz, and contain abundant muscovite and very little feldspar (Sherrill and others, 1941). The heavy-mineral suite is made up chiefly of zircon and tourmaline, and other minerals are rare. The sands are well cemented with secondary silica and minor amounts of calcite, although most of the coarse pebbles are loose or poorly cemented. Thus, the Venango sands constitute a mature quartzite and in this respect differ markedly from some of the older units such as the Bradford Third sand. Krynine (1940) has described the latter as a graywacke, composed of "30 percent of rock fragments, 3 to 4 percent biotite and muscovite, 5 to 12 percent clayey matter (made up largely of small shreds of biotite and sericite), practically no feldspar, and 60 to 65 percent of individual quartz grains." The most abundant heavy minerals are apatite, barite, zircon, and tourmaline.

The Venango sands of the Conewango group are the best known and in gross features at least, may be taken as typical of most of the Upper Devonian marine facies in the Allegheny Plateau region of Pennsylvania. For this reason then, they will be considered in somewhat more detail.

One of the most extensive of these units is the Venango First sand, which extends from the northern district through the middle district, where it is known as the Hundred Foot, to the McDonald area where it is divided into the upper or Gantz sand and the lower or Fifty Foot sand. The Venango First sand is a composite body which is made up of small irregularly shaped sandstone lenses in a shaly matrix. The sandstone lenses occur at different levels within the unit, and correlation of these small bodies across distances greater than 1 or 2 miles has so far proved impossible. In the southwestern and middle part of their extent, the lenses do not have the typical northeast orientation but may lie in any position—the strike commonly being to the northwest. In addition, their shape in plan view may be long and narrow, curved, or even round.

In the vicinity of Titusville (middle district) the sandstone increases in thickness to about 60 feet and is more easily traced. Northward it is nonproductive of oil and gas and contains only fresh water that enters the sandstone from nearby buried glacial valleys. In this northern area, moreover, it seems to take on the northeast trend so typical of the other Devonian beds.

The (Venango) Second sand is divided by a pronounced shale break throughout a considerable part of its extent. In contrast to the First sand, however, this unit is more tabular in shape and is characterized along the northwest side by a fairly straight, sharply defined edge. Traced southeastward from this edge, it thickens rapidly to its characteristic thickness of about 30 feet. The coarser materials lie along the northwest border.

The (Venango) Third sand is characterized by several long narrow northeastward-trending lenses that are generally quite pebbly, especially on their northwestern sides. The lenses are part of a fine-grained sandstone of considerable areal extent. (See Fig. 5)

The form and lithology of these sandstones show rather conclusively the shallow-marine, nearshore origin of the Upper Devonian beds. As Brewer (1928) pointed out, these beds exhibit many of the features of modern shorelines—such as bars, spits, and tombolos. In the case of the Venango First sand, fluvial currents of the delta distributaries may have exercised a major role in shaping some of the beds. Sherrill and others (1941, p. 537) stressed the importance of longshore currents in the formation of the Venango Second sand and suggested that the Venango Third may have formed as a series of offshore bars. A modern analogy was suggested by Lytle (1959, p. 35) as existing in the Rhine delta and the shallow epicontinental North Sea.

The Devonian closed with the readvance of the seas and the deposition of 80-100 feet of the Riceville shale (Fig. 4). Much of this shale bears the red coloration of the terrestrial material from which it was formed.

Mississippian system

The Catskill delta continued to grow westward for a time during the Early Mississippian, depositing the fluvial Murrysville sand. Next to be deposited was the Corry sandstone, which grades westward into the Berea formation. The earliest Corry sediments were deposited in a small bay of the shallow sea; later, a salient of the delta stretched across the bay, and sediments were deposited under lacustrine conditions. Alternate periods of marine and lacustrine deposition occurred throughout Corry time, while farther to the west marine shales and siltstones of the Berea were being laid down. The stratigraphy and paleogeography of these beds have been considered in great detail by Pepper and others (1954) and the reader is referred to their paper for a complete discussion.

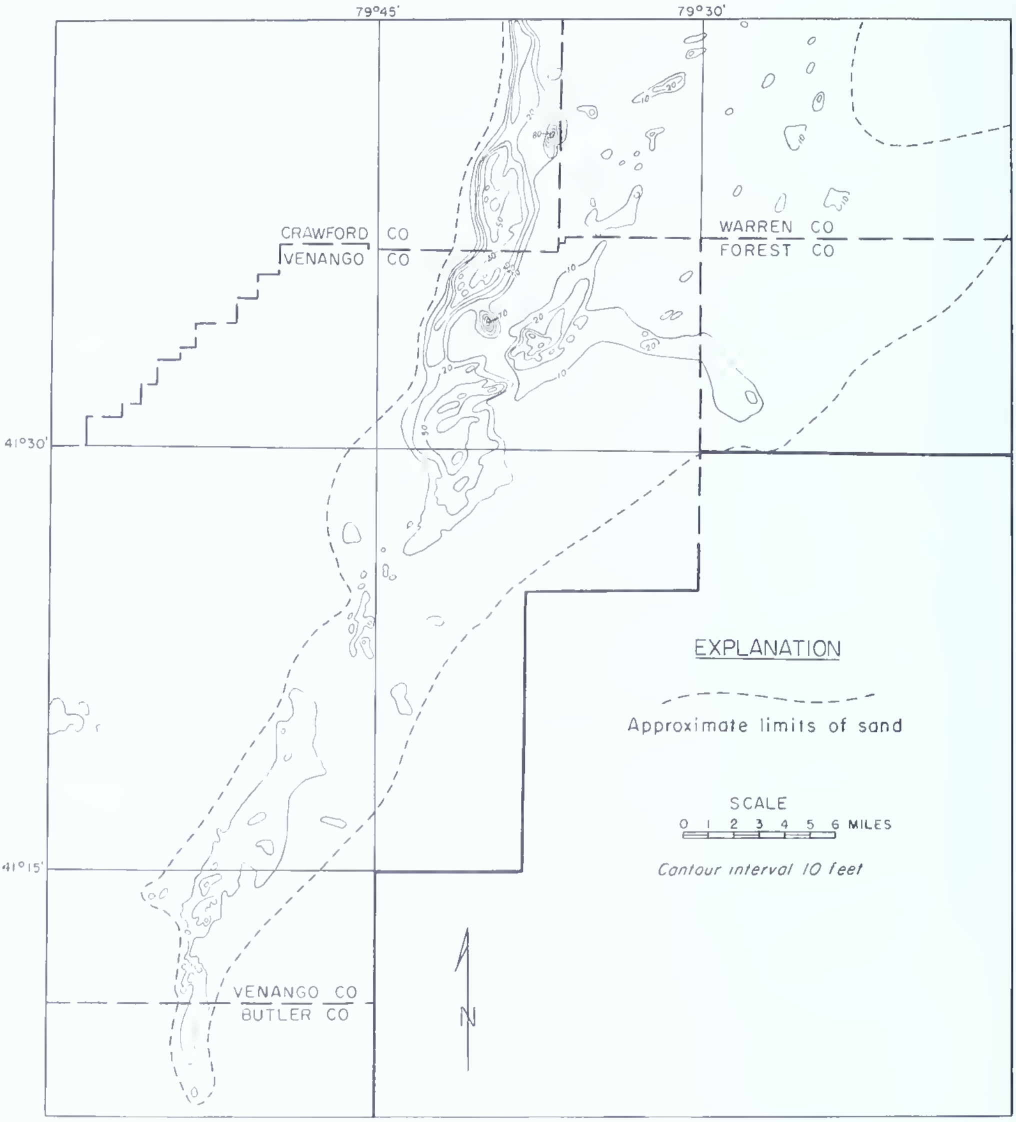


Figure 5. Isopachous map of the Venango Third sand. (After Sherrill and others, 1941).

After Berea and Corry time the sea once more advanced eastward, depositing as much as 600 feet of dark shales, thin-bedded sandstones, and limestones during the remainder of Pocono time. The Pocono group is overlain by the Mauch Chunk red beds in eastern and central Pennsylvania and parts of southwestern Pennsylvania. The Mauch Chunk red beds is more than 3,000 feet thick in the eastern part of the State, though its maximum thickness in western Pennsylvania is not more than 100 feet. Pre-Pottsville tilting of the land surface and subsequent erosion has removed the Mauch Chunk from most of western Pennsylvania. Where the Mauch Chunk is absent, the sandstones of Pottsville age directly overlie the Pocono formation.

Pennsylvanian system

Four groups are recognized as having formed during the Pennsylvanian period. From oldest to youngest they are: Pottsville, Allegheny, Conemaugh, and Monongahela. The youngest group is present in only the southwestern part of the plateau. Successively older beds are exposed to the north, so that in Crawford County the sandstones of the lower part of the Pottsville cap the hills. The Pottsville and Conemaugh are represented by several prominent, massive, quartzose sandstones, whereas the alternate units are characterized by more abundant shales and clayey, silty, micaceous sandstones.

Economically valuable coals occur in all groups of the Pennsylvanian system. The Maxton, Second and First Salt sands, and the First Gas sand are important sources of oil and gas in the southwestern district.

A little more than 1,400 feet of sandstone, shale, and thin limestone was deposited during the Pennsylvanian period in the southwestern part of the State. Most of the clastic sediment was of fluvial origin.

Permian system

By Permian time, the Appalachian basin had nearly filled with sediment. The sea had withdrawn and only a large swampy area remained. Approximately 1,100 feet of the Washington and Greene formations of the Dunkard series were deposited in southwestern Pennsylvania and adjacent parts of West Virginia and Ohio during Permian time. Shales, sandstones, and fresh-water limestones are included, as are some red beds and thin-bedded coals.

STRUCTURE

Throughout most of the Appalachian Plateau the rocks are nearly flat lying; dips rarely exceed a few feet per mile. Only in the eastern part, in a zone transitional to the Valley and Ridge Province, do these dips become steep.

The structure of the Appalachian Plateau was developed through the interaction of three factors. The first factor was the broad, gentle epeirogenic movements which occurred during the Paleozoic era. When major movements of this type have occurred, the event has been recorded in the sediments either by a marked, progressive change in facies or by an unconformity resulting from the emergence of the land followed by temporary cessation of sedimentation or by erosion. During the earliest recorded major Paleozoic unconformity in the Plateau about 4,500 feet of Middle Ordovician and Lower Ordovician limestone and dolomite was removed (Fettke, 1953, p. 73). During early Middle Devonian time widespread emergence and erosion occurred once more. In northwestern Pennsylvania this event is reflected perhaps by the absence of the Oriskany formation, and farther north, in the vicinity of Buffalo, N. Y., the entire Lower Devonian and some of the Upper Silurian beds are missing. A third major unconformity was developed during Late Mississippian and Early Pennsylvanian time, as discussed earlier.

The second factor in the structural development of the Appalachian Plateau is its position on the western flank of the Appalachian geosyncline. The sediments dip and thicken eastward toward the axis of deposition and the dip increases from the youngest to the oldest beds.

The third factor is the deformation that occurred during the Appalachian orogeny, at the close of the Paleozoic. It was at this time that the major folds and faults were developed in the Valley and Ridge province and the adjacent parts of the Plateau. Fettke (1954, p. 7) states:

> ...the foreland folds are best developed in Fayette, Somerset, and Westmoreland Counties in a belt nearly 50 miles wide. Individual folds have a width of from 8 to 10 miles from syncline to syncline, and domes along the anticlinal axes rise from 2,000 to 3,500 feet above adjacent synclinal lows. ...En echelon offsets are fairly common. In southwestern Pennsylvania, in Fayette County, the folds trend approximately N. 30° E. In a northeastern direction they gradually swing to the east in a broad arc until in north-central Pennsylvania, in Tioga County, the trend is N. 70° E . . . where the bend is sharpest, the foreland folds are cut by a series of transverse faults.

Subsurface investigations have shown far more complex structure than was evident from surface studies, as illustrated in Figure 2 by structure contour lines on top of the Oriskany formation. Displacements of as much as 1,800 feet have been encountered. Thus, referring to the Chestnut Ridge anticline, Fettke (1954, p. 8) states:

> "A series of four exploratory wells, drilled across the axis of the fold revealed the presence of a drag fold in the form of an anticline over-turned toward the southeast. One of the wells passed through the Oriskany sandstone three times in an interval of 1,800 feet."

The folds, to be sure, die out fairly rapidly toward the northwest, so that over most of the Plateau the structural features are due to the first two factors discussed above.

HYDROLOGY

Occurrence of Brine

Information on natural brines has been obtained almost exclusively from oil and gas wells. In Upper Devonian and younger formations, the areal distribution of the oil and gas fields has been restricted to a narrow belt approximately coinciding with the sandstone lenses described earlier; thus, knowledge of the extent of the occurrence of the brines has been restricted similarly. Below the Tully limestone, as noted earlier, interest has centered on the Oriskany formation. In Pennsylvania as a whole, then, information on the brines is restricted areally and stratigraphically.

Brine has been found to occur both as "free" water in the interstices of the rock and as moisture adsorbed on the grains of the rock. If the pores contain enough water and are sufficiently large and interconnected to allow the water to move readily when a pressure differential is applied, the water is termed free. Where these conditions are lacking, the moisture is adsorbed as a thin film around the grains.

Adsorbed water is firmly held by the rocks. It will not drain by gravity; it is held by molecular attraction against evaporation; and it is not displaced by oil. In the last instance it may be considered to serve as a lubricant facilitating the flow of oil.

Parts of some of the Upper Devonian and Mississippian formations contain very little or no water, despite the fact that studies have shown the strata to be porous and permeable. Most of the water that occurs in these "dry sands" is present as adsorbed moisture. Many theories have been advanced to explain this situation. The most satisfactory are those of Reeves (1917) and Mills and Wells (1919). Reeves noted the close association of the "dry" strata with red beds and suggested that the sediments had been dried out subsequent to deposition and that air entrapped in the pores had prevented water from reentering the rocks. The theory was considered plausible and was widely accepted. Torrey (1934a, p. 469), however, states that the discovery in recent years of marine fossils in cores of some of the "dry sands" has tended to discredit the theory. A slight retreat of the sea following deposition of the sediments, nonetheless, could have resulted in exposure and desiccation of the shallow marine beds.

Mills and Wells (1919) ascribed the desiccation of the sandstones to evaporation of the water into moving and expanding gas. Torrey (1934a) has used this concept as a nucleus on which to build an elaborate theory of the origin and occurrence of oil, gas, and water in the Appalachian basin. Noting the proximity of the "oil sands" to shales rich in organic matter, he suggests that the oil and gas formed in the shales soon after the deposition of the sediments and migrated into the sands prior to their consolidation. The gas was generated first and in greater quantities closer to the shoreline. As it moved through the unconsolidated sands and escaped into the air, sea water initially trapped in the pores was evaporated. If drying was complete, the mineral content of the water was left as an encrustation on the sand grains. Compaction and cementation of the sediments and formation of a cap rock prevented the escape of all the gas. Where gas is found today in these formations, it is accompanied by little or no water, although salt crystals are found frequently in the pores in the rock. In some places where fresh water has entered these beds through leaky casings or poorly plugged wells, it has been found to be fully as salty as the natural brine when it is returned to the surface.

In the offshore-bar deposits, farther down the primary dip, the gas was abundant enough only to concentrate the brine somewhat as it passed through the pores. Consequently, where oil is present, it is produced with copious amounts of water and with little if any gas. "In fact," Torrey (1934a, p. 467) states, "[oil] wells that produced little or no water were soon exhausted, so that the presence of water in the sand, rather than being a necessary evil, has had highly beneficial effects on the ultimate yield of oil."

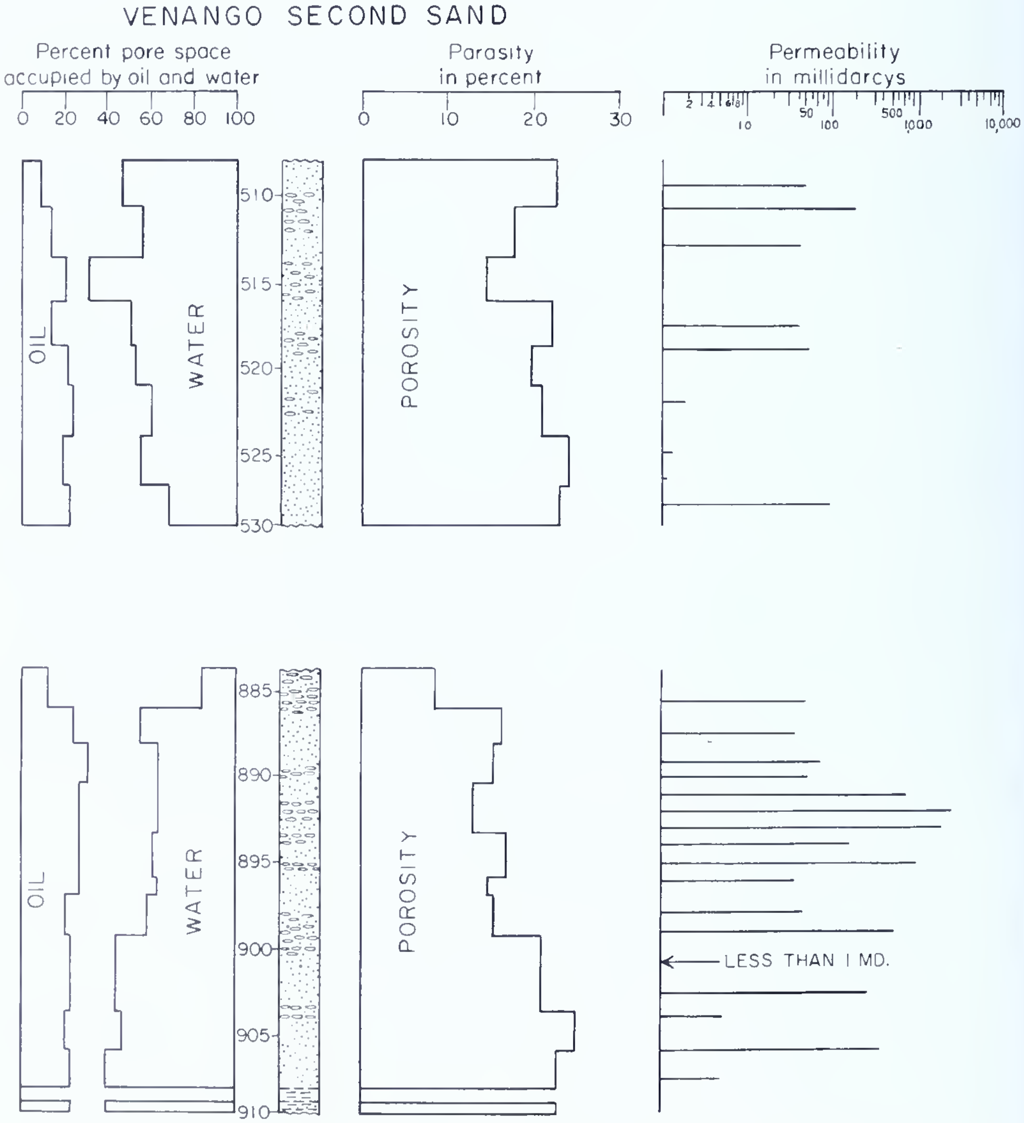


Figure 6. Profiles showing porosity, permeability, and oil and water content of Venango Second sand near Oil City, Pennsylvania. (After Sherrill and others, 1941).

Either theory, therefore, points out the decrease in the amount of water that may be expected toward the old Upper Devonian or Mississippian shorelines. The offshore sands may be expected to yield larger amounts of water, depending on the storage capacity of the formation.

Inasmuch as the shoreline shifted back and forth with time, the maximum yields from the different oil sands occur in different places. Thus, the Hundred Foot sand yields large amounts of water throughout most of its extent, though there is a general absence of water in the formation in Beaver and western Allegheny and Washington Counties (Reeves, 1917, p. 372). The Venango Third and Fourth sands are dry or nearly so in Butler County (Torrey, 1934a, p. 469).

Well-defined gravitational separations of gas, oil, and water are rarely observed in Upper Devonian or younger beds in the Appalachian basin because of the low dip of the beds, and the lenslike character and erratic cementation of the sandstones. Perhaps the best example of such a separation is the anticlinal accumulation of oil in the Bradford oil field. The situation is not a simple one for, despite the removal of several hundred million barrels of oil over a period of more than half a century, there has been little encroachment of the edge and bottom waters. The phenomenon is due to a marked decrease in the permeability (due to cementation downdip, toward the edge of the field) which developed apparently after the emplacement of the oil. Restricted permeability great enough to offset the effect of structure occurs also on the Smethport anticline in northwest Potter County, where gas occurs below the oil (Torry, 1934a, p. 477). The percent oil and water saturation, percent porosity, and irregular permeability throughout a vertical section of a typical oil sand is shown in Figure 6.

Structural control of gas is usually more effective. As a matter of fact, the anticlinal theory of accumulation of oil and gas first became well known as a result of I. C. White's (Levorsen, 1954, p. 140) investigation of the occurrence of gas in the Appalachian province. It has recently been used in the location of gas in the older formations in the eastern part of the Allegheny Plateau.

HYDRAULICS

Ground water may occur under either nonartesian (water table) or artesian conditions. The first condition occurs where the water level is free to rise or fall in permeable material; the upper surface of the ground water is called the water table. Artesian conditions occur where the water is confined under pressure in a permeable bed that is overlain by a relatively impermeable bed so that the water surface is not free to rise and fall.

If a well is drilled into a water-table aquifer, the water level in the well will stand at the same level as in the formation. As the water is pumped out of the well, the aquifer will be partly dewatered and the emptied pores filled with air.

In a well drilled into an artesian aquifer, the water level will rise above the aquifer by an amount dependent on the height of the water table in the outcrop area and the efficiency of transmission of the hydrostatic pressure, from the outcrop to the place where the water enters the well. The initial effect of pumping the well will be a lowering of the head in the aquifer. As the water is removed, the aquifer will compress and the pore space will be decreased slightly. When pumping stops, water flowing from more distant parts of the aquifer to the vicinity of the well soon restores the water level to its original state. The removal of sufficient water could result in dewatering and, as in the first situation, the pores being filled with air.

The yield of a well drilled into an aquifer depends mainly on the aquifer's thickness and permeability.

The same principles apply to brine aquifers, with certain modifications. First, there is no recharge of brine to the aquifer other than the very small amounts that may drain from contiguous shales. The total amount of brine that may be obtained from an aquifer is limited, therefore, and the production of brine must be considered a mining operation in the same sense as that of oil, gas, or metallic ores. It has been demonstrated in a number of small fields that the supply of brine can be depleted over a period of years.

Second, brine aquifers differ from fresh-water aquifers by their lack of appreciable circulation. Near stagnation has been established in the brine aquifers because they are confined below local points of discharge. Depths to the top of the producing formations in the wells sampled range from 650 feet below land surface in a well drilled into the Berea sandstone in Lawrence County to more than 7,500 feet in a well that tapped the Oriskany formation in Clearfield County. The upper surface of the Berea is at 500 feet above sea level, and the upper surface of the Oriskany is nearly 5,900 feet below sea level at these wells.

Third, the height to which the water will rise in the well will be governed not only by the hydrostatic pressure due to the weight of the overlying rocks and water, but also to the presence of any gas. For instance, the gas pressure in one well that was drilled to a depth of about 7,500 feet in the Oriskany sandstone caused the water to flow from the well. Because of the lack of gas pressure in two nearby wells that were drilled into the same formation, to approximately the same depth, the water level was 800 to 900 feet below land surface. Much less spectacular examples are common, but the presence of gas in even minor amounts is sufficient to affect the static water level and to invalidate the application of the methods used in the study of the hydraulic properties of fresh-water aquifers.

Water-level measurements in wells tapping the brine-bearing aquifers are difficult to obtain because few wells are being drilled and the pump installations on the older wells do not allow access to the water surface.

Table 3. *Summary of statistics showing the relationship of density, specific conductance, chloride, bromide, sodium, calcium, magnesium, potassium, and strontium to dissolved solids*

a.—(The dissolved-solids content (X), in parts per million, is the independent variable and the other variables (Y) are the dependent variables in a linear equation $Y = a + bX \pm S_y$)

	Number of samples	Slope b	Y-intercept a	Standard error of estimate S_y	Coefficient of correlation r
Density (g per ml @ 20° C.)	51	7.52×10^{-7}	0.992	0.0049	0.9966
Specific conductance (micromhos at 25° C.)[1]	51	450.	−21,900	8,630	0.9851
Chloride (ppm)	51	0.5466	1,300	2,970	0.9976
Bromide (ppm)	51	0.004919	−64.8	158	0.9248
Sodium (ppm)	35	0.2454	560	3,340	0.9938
Calcium (ppm)	35	0.08179	−754	1,880	0.9825
Magnesium (ppm)	35	0.01229	69	205	0.9173
Potassium (ppm)	35	0.00115	36.1	102	0.3975
Strontium (ppm)	35	0.000966	3.91	51	0.7573

[1] Specific conductance is related here to the square root of the dissolved-solids content, $SC = a + bDS^{1/2} \pm S_y$.

b.—(The dissolved-solids content (X), in parts per million, is the dependent variable and the other variables (Y) are the independent variables in a linear equation $X = a' + b\,Y \pm S_X$.

	Number of samples	Slope b′	X-intercept a′	Standard error of estimate S_X	Coefficient of correlation r
Density (g per ml @ 20° C.)	51	1,320,900	−1,309,500	6,450	0.9966
Specific conductance (micromhos @ 25° C.)[1]	51	0.002157	57.36	13,460	0.9851
Chloride (ppm)	51	1.8206	−1,744	5,420	0.9976

[1] Specific conductance is related here to the square root of the total dissolved solids, $DS = (b'SC + a')^2 \pm S_X$.

The amount of brine which may be produced from a formation can be estimated from core tests of permeability and percent fluid saturation (Fig. 6). However, such studies were not made in this investigation. Reasonable estimates of the maximum potential yield of wells cannot be made because the pumps presently used on the brine-yielding wells are of low capacity, designed for the slow movement of the oil into the wells. The oil-water production ratio of active oil wells varies widely. Some wells may produce little or no water, although one in Allegheny County, in the Hundred Foot sand, produces 90 barrels of water to 1 of oil (Lytle, 1950, p. 91).

GEOCHEMISTRY

Analysis of the Data

Quantitative determinations of 24 constituents were made as part of the analysis of the brines, although some constituents—such as cesium and rubidium—were determined for only a few samples. The dissolved solids content of the samples was obtained by calculating from the determined constituents and by evaporating the residue at 180° C. In addition, such properties as the specific conductance, pH, and density were measured.

The results of the analyses will be discussed under the following four groupings: (1) Dissolved solids, density, specific conductance, and pH; (2) the major constituents—chloride, sodium, calcium, and magnesium—which were present in amounts usually in excess of 1,000 parts per million (ppm); (3) the minor constituents—bromide, potassium, strontium, and barium—which rarely exceeded 1,000 ppm; (4) the trace constituents—silica, iron, manganese, copper, lithium, fluoride, iodide, and nitrate—which were present in most samples; and aluminum, zinc, and phosphate, which were absent from a large number of the samples. Bicarbonate, which ranged widely in content and sulfate, reported as 0.0 ppm (less than 0.05 ppm) in all but two samples, will be discussed with the fourth group. The trace constituents seldom exceeded a few tens of parts per million.

The concentrations of the major and minor elements, except barium, and the conductance and density of the water show a definite relationship to the dissolved solids content. Summary statistics describing the relationship are given in Table 3 and will be discussed in their respective sections. The coefficients of this table were computed with the following relationships:

$$b = \frac{\left[\Sigma\left(X - \frac{\Sigma X}{N}\right)\right]\left[\Sigma\left(Y - \frac{\Sigma Y}{N}\right)\right]}{\Sigma\left(X - \frac{\Sigma X}{N}\right)^2}$$

$$a = \frac{\Sigma Y - b\Sigma X}{N}$$

$$S_y = \sqrt{\frac{\Sigma\left(Y - \frac{\Sigma Y}{N}\right)^2 - b^2\,\Sigma\left(X - \frac{\Sigma X}{N}\right)^2}{N - 2}}$$

$$b' = \frac{\left[\Sigma\left(X - \frac{\Sigma X}{N}\right)\right]\left[\Sigma\left(Y - \frac{\Sigma Y}{N}\right)\right]}{\Sigma\left(Y - \frac{\Sigma Y}{N}\right)^2}$$

$$a' = \frac{\Sigma X - b'\Sigma Y}{N}$$

$$S_x = \sqrt{\frac{\Sigma\left(X - \frac{\Sigma X}{N}\right)^2 - b'^2\,\Sigma\left(Y - \frac{\Sigma Y}{N}\right)^2}{N - 2}}$$

$$r = \sqrt{b\,b'},$$

where b is the slope of the linear equation of the form $Y = a + bX$, a is the Y-intercept of that equation, and S_y is its standard error of estimate.
b' is the slope of the linear equation of the form $X = a' + b'Y$,
a' is the X-intercept of that equation, and S_x is its standard error of estimate.
r = the coefficient of correlation.
X is the concentration of the dissolved solids in the residue in ppm in each sample.
Y is the value of the density, chloride, and/or other constituent in the same sample.
N is the number of samples.
The standard error of estimate (S_y) offers a measure of the scatter of the data around the regression line. For example, if the dissolved-solids content of a brine were known to be 100,000 ppm, the chloride content could be estimated as follows:

$Cl = 1{,}300 + 0.5466(100{,}000) \pm 2{,}970 = 55,960 \pm 2{,}970$ ppm

Therefore, if the dissolved-solids content of the brine is 100,000 ppm, the true chloride content may be expected to lie between 53,000 and 57,900 ppm about two-thirds of the time. If greater confidence is required, the use of $\pm 2\ S_y$ will insure that the true value lies within the interval about 95 times out of a 100; or with $\pm 3\ S_y$ the confidence level is raised to 99.74 percent. The coefficient of correlation (r) shows the degree of relationship between the two variables.

The variation in number of samples shown in table 3 is discussed in the section dealing with each ion.

PROPERTIES OF THE BRINE

The dissolved-solids content of the brine, as indicated above, was determined by two methods: (1) calculated from the determined constituents, and (2) residue upon evaporation at 180° C to dryness.

One of the most impressive features of the brine is its relative uniformity of composition regardless of concentration, age, geologic horizon, or geographic location in Pennsylvania. As a result, the dissolved-solids content may be estimated quite easily and inexpensively by measuring the density of the solution. A closer but more expensive estimate may be obtained from the chloride content of the sample. Figure 7 shows the relation of density and chloride to dissolved solids. The chloride versus dissolved solids plot shows no change in the amount of scatter of points toward the higher values, while that of the density versus dissolved solids shows these higher values to lie consistently above the line; that is, these samples have a higher density in proportion to their concentration than the average sample. These relations indicate that the anion composition is unchanged, but that there is a substitution of heavier cations (especially calcium for sodium) which make up the brine at lower concentrations.

The higher than average density at higher dissolved-solids concentrations is in large part responsible (by changing the slope of the regression line) for a density of 0.992 at a zero dissolved-solids concentration. The density to be expected at the temperature at which measurements were made (20° C) is 0.998.

As a first approximation, the specific conductance of a solution is proportional to the square root of the concentration. Such a plot is shown in Figure 8.

The negative logarithm of the hydrogen ion activity is termed the pH and is a measure of the acidity ($pH < 7$) or alkalinity ($pH > 7$) of the solution. The pH of a solution is a function of the equilibria established by the several ions in solution, and in the brine, as in most natural waters, the presence of the bicarbonate ion exerts a strong effect on the pH. Bicarbonate was present in all the brine samples having pH greater than 4.5 and reached a maximum of 583 ppm in the sample having the highest pH value (7.8), the brackish water of the Salt sand in well 703. Only five samples had pH of less than 4.5; two of these were from the Mountain sand, two were from the Murrysville sand, and one was from the Gordon sand. The lowest pH value was 3.85 from well 222 in the Mountain sand. The cause of these low pH values is not known, but it may be due to dissolved gases or to local lithologic factors.

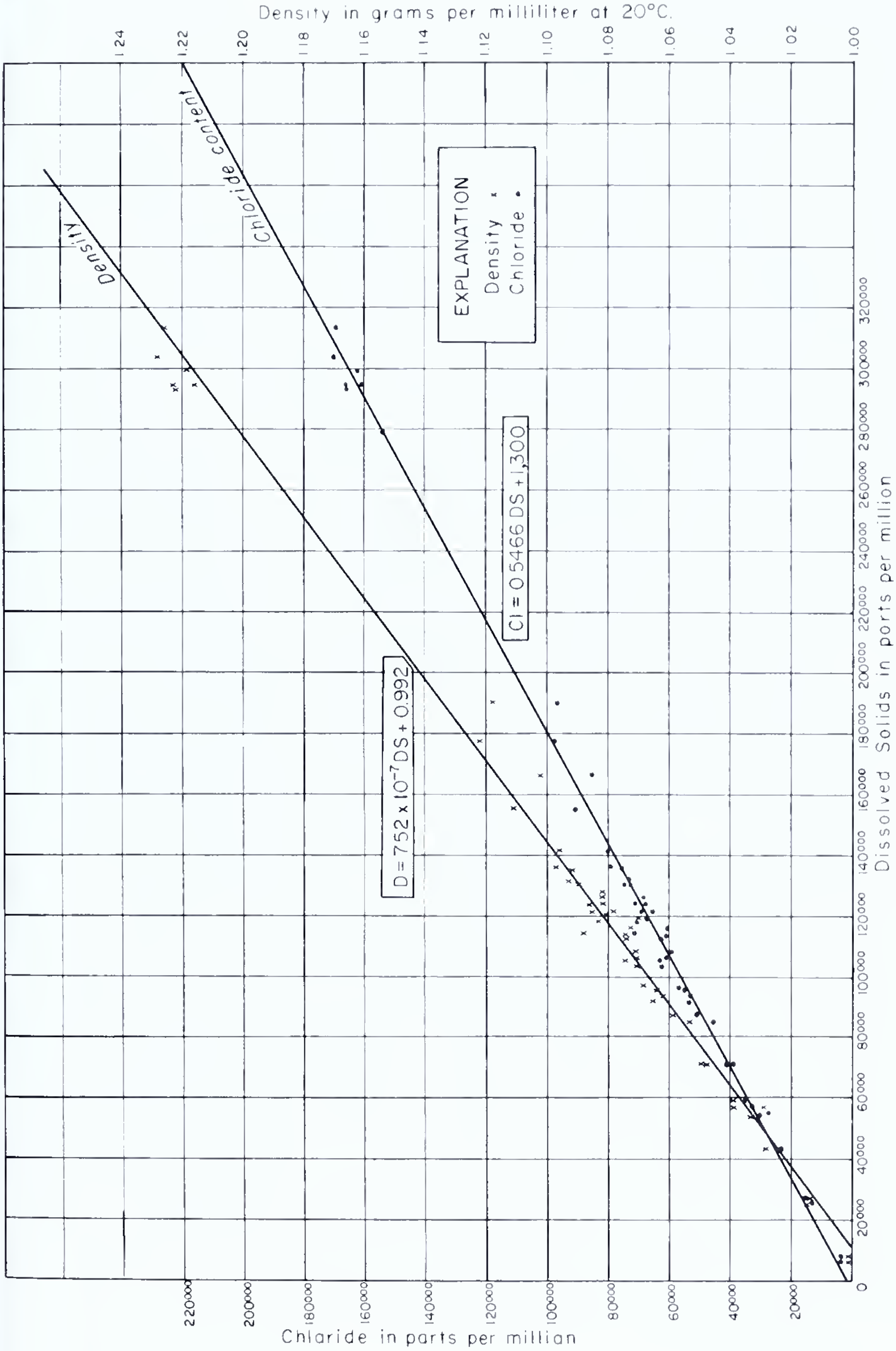


Figure 7. Graph showing relation of density and chloride to dissolved-solids.

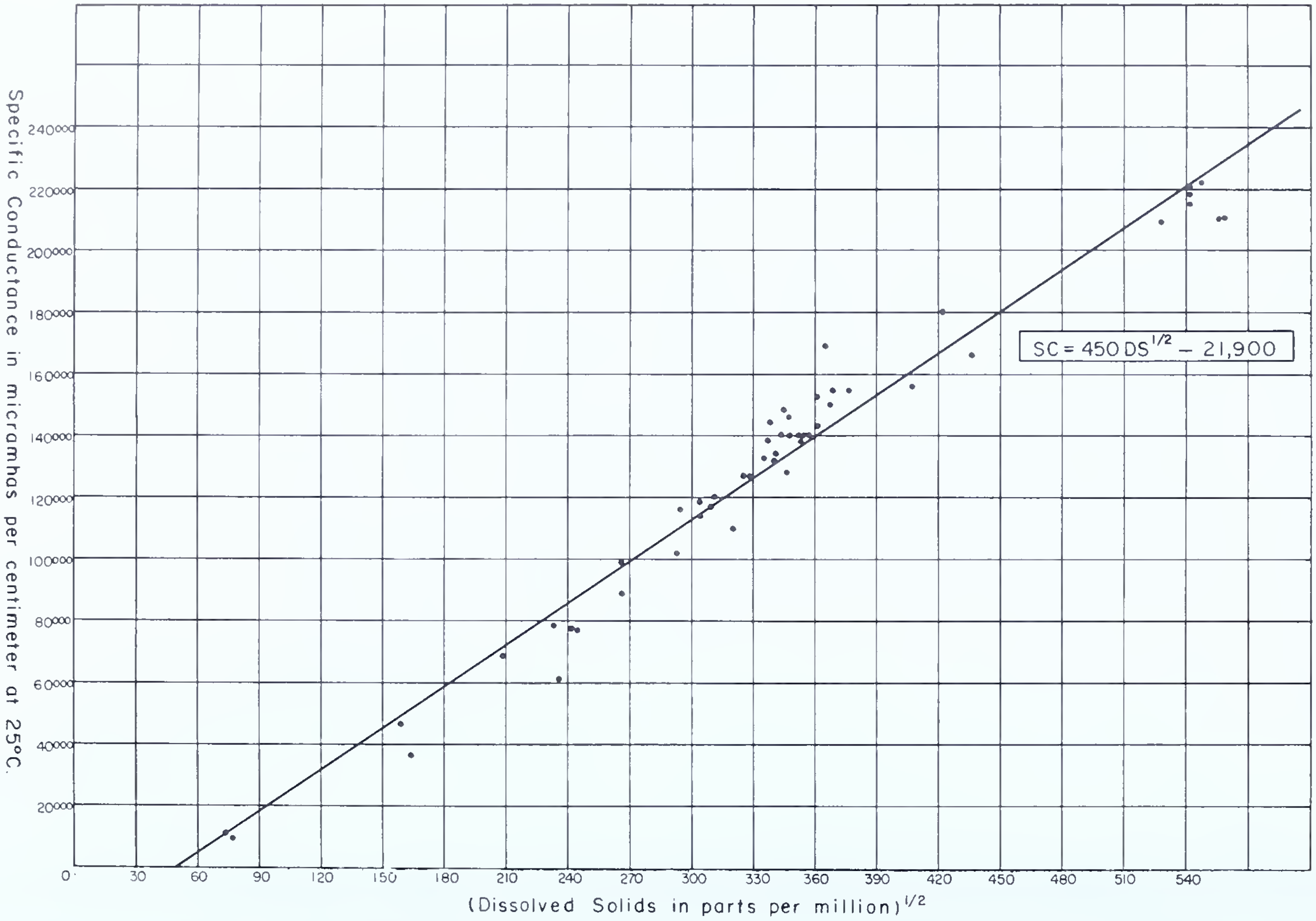


Figure 8. Graph showing relation of specific conductance to the square root of the dissolved-solids.

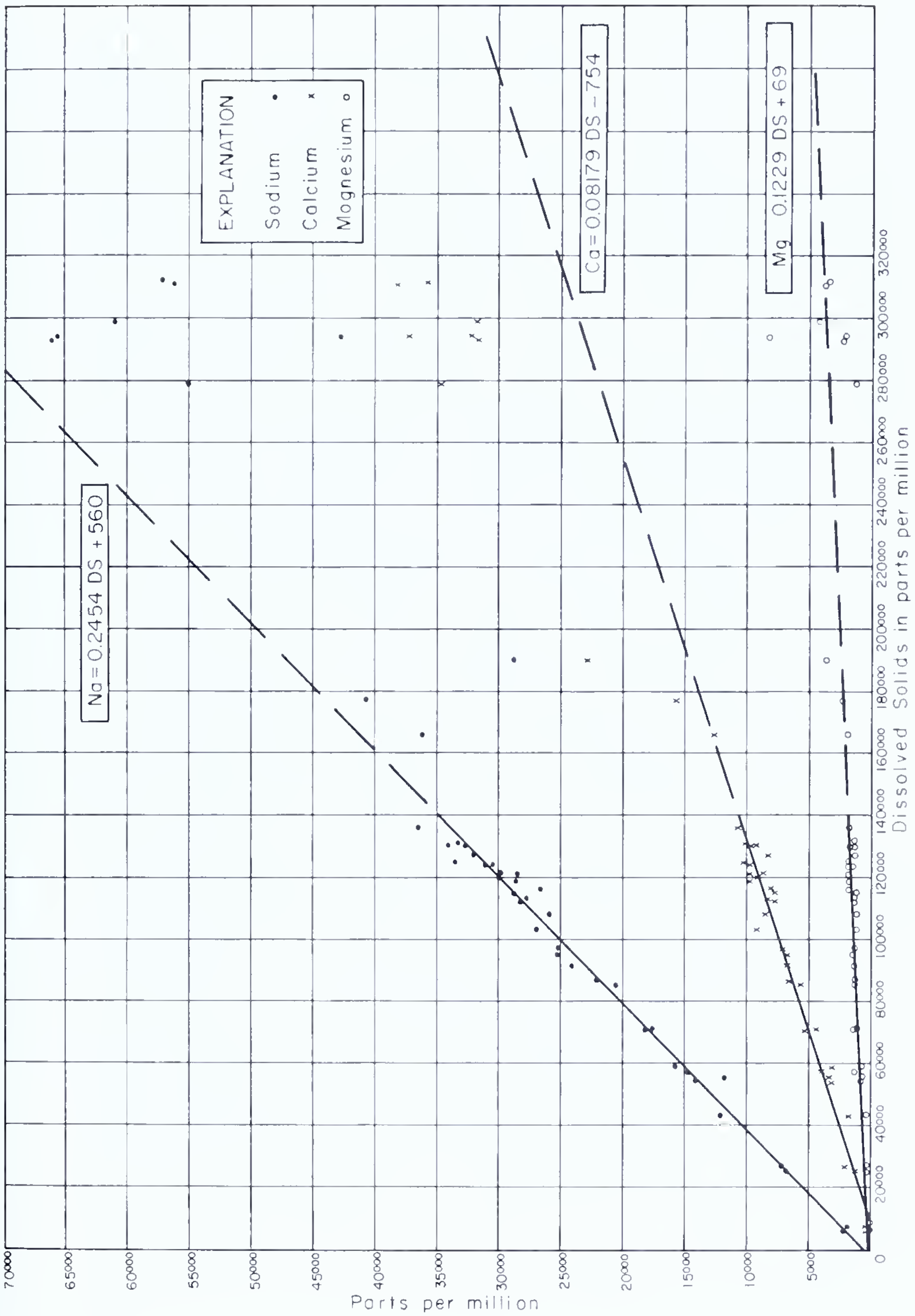


Figure 9. Graph showing relation of sodium, calcium, and magnesium to dissolved-solids.

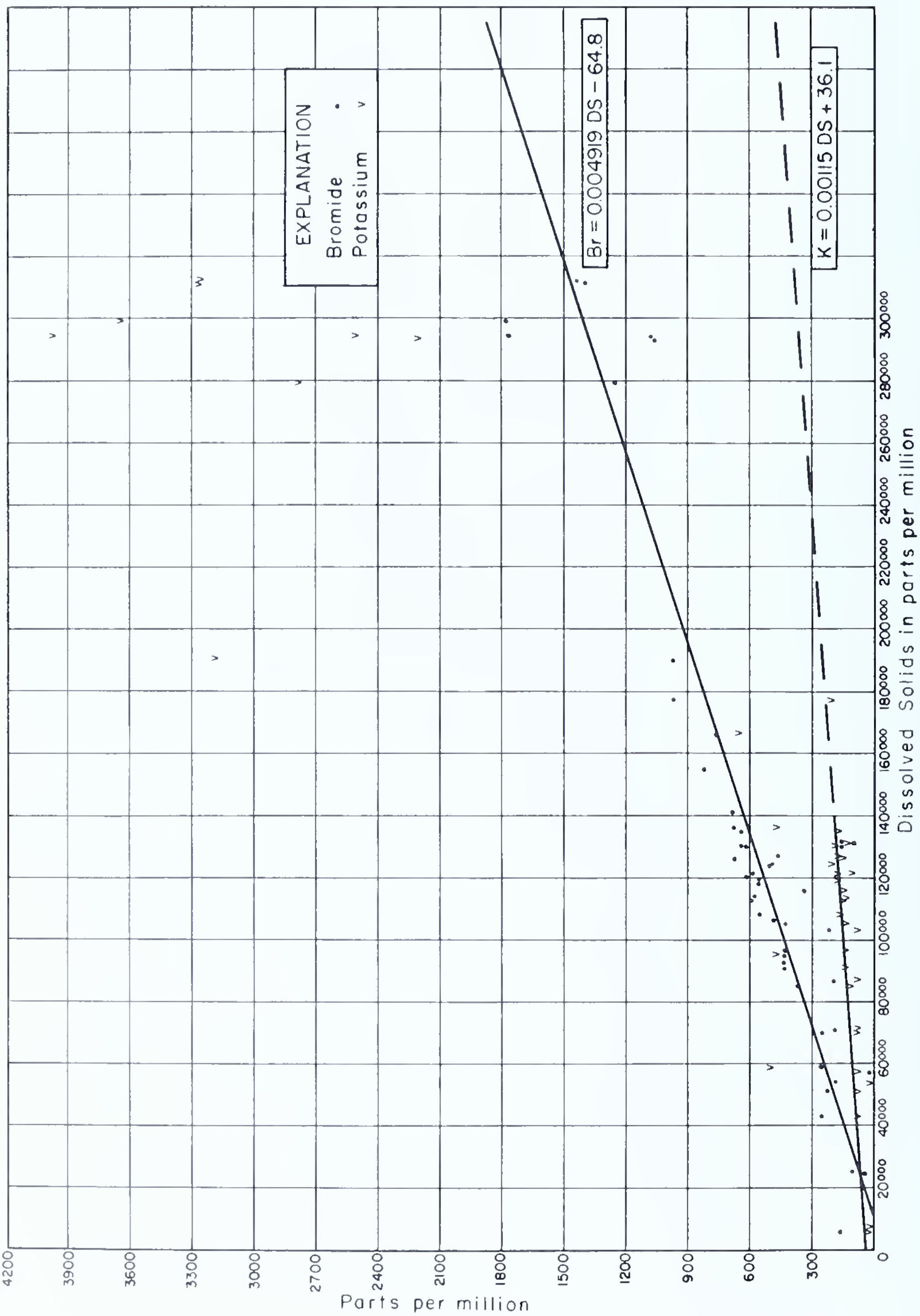


Figure 10. Graph showing relation of bromide and potassium to dissolved-solids.

MAJOR ELEMENTS

Chloride (Cl) was by far the most abundant constituent in the brine, making up nearly 50 percent of the dissolved solids in each sample in percent equivalents. None of the other anions exceeded 0.20 percent. Because of the small scatter of points about the chloride-dissolved solids (see figure 7) regression line throughout the full range of the data, the dissolved-solids content offers an excellent estimate of the chloride content with a standard error of estimate of less than 3,000 ppm. The relation shows no evidence of ion exchange.

The regression lines of sodium (Na), calcium (Ca), magnesium (Mg), and potassium (K) to dissolved-solids were computed with only the 35 samples having less than 140,000 ppm solids. This was done to emphasize the change in the proportions of the ions at the higher concentrations and to improve the correlation of the data with the computed line. These computations will aid in estimating the amounts of the ions from the solids at the lower concentrations. This particular "cut-off" point was selected because the data are considerably less abundant and the scatter is greater above this point. The data were not sufficiently abundant at the intermediate concentrations to allow the computation of a curve encompassing all the data.

Inspection of Figure 9 shows that the more concentrated solutions contain markedly less sodium and more calcium than normally expected by the regression equation. Potassium content, in particular, is higher than predicted in these solutions. (See Fig. 10.) Data on magnesium in solutions containing more than 140,000 ppm of total solids are characterized by an increased scatter.

Ion exchange may be defined as the "replacement of ions adsorbed on a solid, or exposed at the surface of a solid, by ions from solution" (Howell, 1957, p. 154). The reaction takes place almost instantaneously and is due to a number of factors. In the case of the solid, the ion-exchange capacity is due to the number of unsaturated charges on the individual particles. These in turn may be due to broken bounds along the noncleavage edges of the particles, and, hence, the total number in a unit volume of material will increase with decreasing particle size. Substitution of aluminum for silicon in the tetrahedral sheets and of magnesium for aluminum in the octahedral sheets in the lattice of certain minerals, especially the clays, is often quite important in increasing the exchange capacity. These substitutions are found mostly on the cleavage surfaces. The hydrogen of hydroxyls exposed along the broken edges of the lattice also may be exchanged (Grim, 1953, p. 132–133). In the solution, the charge on the ions, their hydrated ionic radii, and their concentration are important in determining the nature of the reaction. The replaceability is, thus, seen to depend both on the material and the solution, and the order from the standpoint of the solid is essentially that given by Way, (Kelley, 1948, p. 57) as follows:

$$Na < K < Ca < Mg < NH_4 \cdot$$

This order indicates, for example, that in general the solid will extract calcium ions from solution and replace them with sodium ions. The reaction is reversible, however, and Schubert (1959, v. 12, p. 573C) in discussing synthetic exchange resins, states that in concentrations "above 3 molar, the resins may have a greater affinity for ions of lower charge." As a first approximation, this seems to hold for natural materials.

MINOR ELEMENTS

The elements of this group with the exception of potassium are not usually determined in a chemical analysis of water. Bromide, a member of the halogen family, reacts similarly to chloride and, hence, is commonly determined with the chloride. For the same reason, potassium may be lumped with sodium and, together, they are called total alkali. Strontium and barium are determined with calcium and the three are referred to as alkaline earths.

Bromide shows a good correlation with dissolved solids. Its concentration can, therefore, be estimated from the latter with a standard error of estimate of 150 ppm. Figure 10 shows an increased scattering of the bromide data with increased concentrations indicating the increased effect of some variable (s). The exact cause is unknown.

The poor correlation of potassium with dissolved solids (based on samples containing less than 140,000 ppm is due, in large part, to the effect of three samples, all of which show marked deviations from the regression line (greater than 2.2 S_y); in each sample the potassium is greater than estimated by the regression line. Deletion of these three analyses from the calculations of the correlation coefficient would more than double the coefficient.

One sample (well 226) is from the Hundred Foot sand in northern Butler County; the other two samples (wells 705, 707) are from the Gordon sand in Washington County. These samples, which are represented by partial analyses only, show no abnormality in the concentrations of the other ions.

Except for the samples having dissolved-solids content of approximately 300,000 ppm only two other potassium values deviated significantly from the regression line. One was from the Gordon sand (well 603) in Allegheny County and the other from the Salina formation (well 1201) in Erie County. The concentrations of all the cations are significantly different in the Salina sample and the differences are probably due to the presence of evaporites in the formation. The high potassium content might offer a means of identifying water from the Gordon sand. Although the information available is inadequate for further analysis, it seems safe to conclude that the deviations are probably due to unknown lithologic factors.

Only 35 samples were analyzed for strontium (Sr) content and all were included in the computation of the regression and correlation coefficients of strontium with total solids. (See Fig. 11) Two samples depart significantly from the regression line: (1) number 101 from the Berea has a positive deviation of 4.05, and (2) number 701 from the Gordon sand has a negative deviation of 2.05.

Barium (Ba) content was determined in 28 samples. A plot of barium versus dissolved solids is shown in Figure 11. The lack of correlation between barium and dissolved solids is quite evident. There is also a lack of correlation between barium content and the geologic source of the sample. The concentration ranges widely and erratically from a low of 1.9 ppm for a sample from the Salt sand (well 703) to 1,080 ppm for one from the Berea. Heck (1940) discussed the occurrence of barium in Appalachian brines and suggested that the barium was originally present as barite in the formation and was brought into solution at the time the sulfate was reduced. The subsequent introduction of sulfate-bearing meteoric waters apparently has been responsible for the precipitation of the barium in some parts of West Virginia. Similar conditions may explain some of the low concentrations in Pennsylvania brines.

TRACE ELEMENTS

These constituents may be divided conveniently into two groups: (1) silica, iron, manganese, copper, lithium, fluoride, iodide, and nitrate, which were present in all or most of the samples, and (2) aluminum, zinc, phosphate, bicarbonate, and sulfate, which were detected in measurable quantities in only a few samples. These elements are independent of the total concentration of the brine and seem to bear little, if any, relation to the geologic formation from which the sample was taken. The first group is summarized in Table 4.

Table 4. *Summary of statistics of selected trace constituents*

	Number of samples	Median (ppm)	Range (ppm)
Silica (SiO_2)	36	9.6	3.1-44
Iron (Fe)	35	52	.13-286
Manganese (Mn)	37	1.8	.03-38
Copper (Cu)	36	.28	0-2.8
Lithium (Li)	33	6.8	0-219
Iodide (I)	51	13	.8-36
Fluoride (F)	37	.7	0-21
Nitrate (NO_3)	33	49	0-118

Nitrogen was reported as nitrate and represents the nitrogen that may be present as nitrate, nitrite, or ammonium salts.

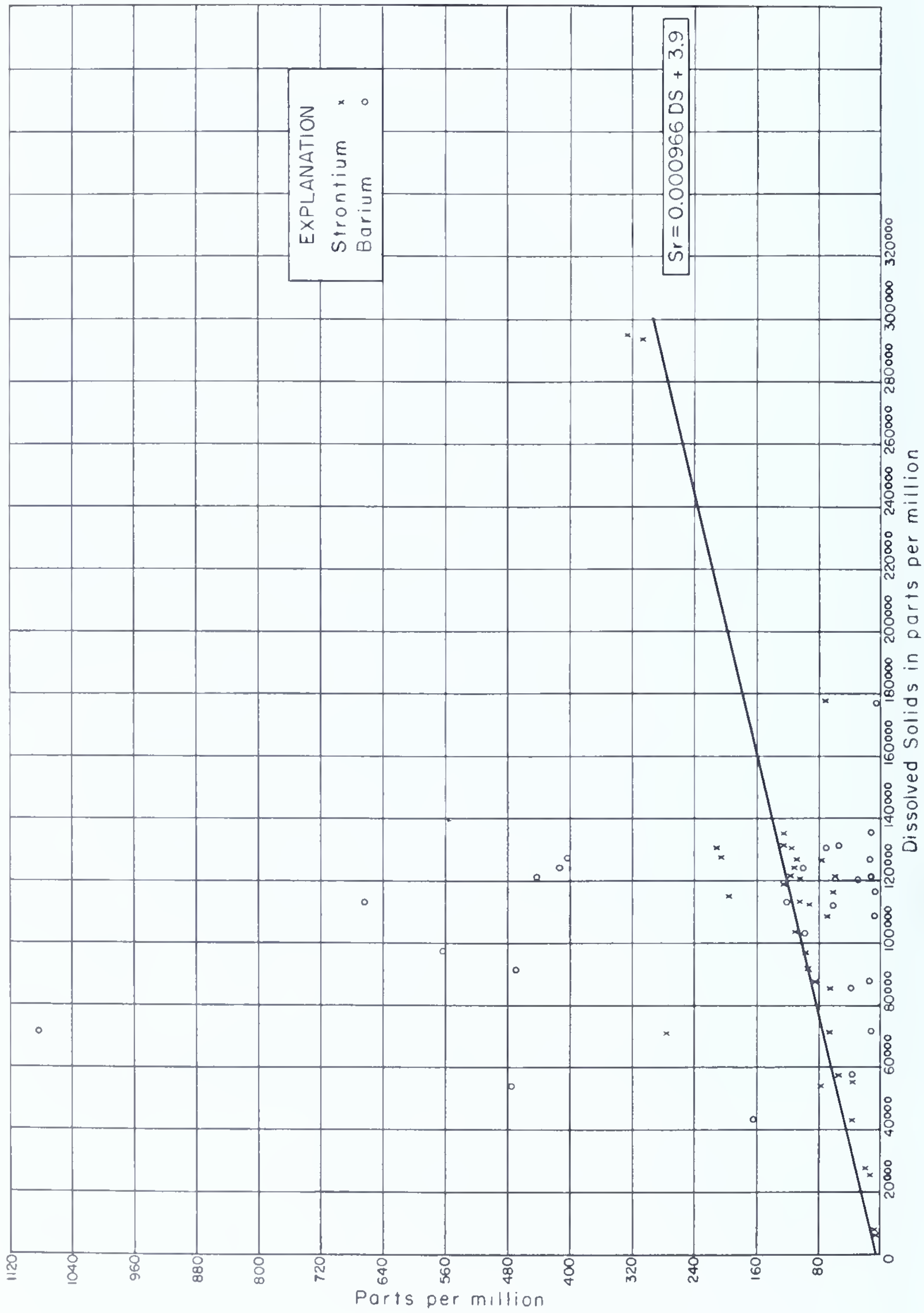


Figure 11. Graph showing relation of strontium and barium to dissolved-solids.

Aluminum, zinc, and phosphate were present in measurable quantities in 14, 14, and 9 samples, respectively, out of 35 in which they were sought. Where detected the aluminum ranged from 0.1 to 1.7 ppm except in one sample that contained 30 ppm; zinc ranged from 0.06 to 13 ppm; and phosphate ranged from 0.1 to 0.2 ppm in seven samples and was present in concentrations of 1.7 and 5.3 ppm in two others.

As indicated in the discussion of pH on page 26, bicarbonate (HCO_3) increased (as the pH increased) from zero ppm at pH 4.5 to a maximum of 583 ppm at the highest pH (7.8). The presence of bicarbonate in a brine is often taken as indicative of contamination by meteoric water. This criterion must be used with caution, however, and in conjunction with other tests, because the presence of carbonate minerals in the aquifer may result in notable contributions of bicarbonate to the solution. Well 1202 in the Gatesburg formation is such an example. Rankama and Sahama (1950, p. 341) point out that carbon dioxide may be formed by hydrocarbon-oxidizing bacteria utilizing the oxygen in sulfates.

The absence of sulfate in oil-field brine is a common phenomena and has resulted in considerable speculation in the literature. Several theories have been offered in explanation. Grimsley (cited by Case and others, 1942, p. 869) suggested that the sulfate had been precipitated by barium chloride. Engler and Hofer (cited in Rogers, 1919, p. 27) suggested that the sulfate was reduced by hydrocarbons to sulfide, which then escaped as hydrogen sulfide gas. An equivalent part of the oil or gas was oxidized to carbon dioxide. Such a reaction has been observed in organic muds from the bottom of rivers or the sea and an abundance of sulfides has been found in aquifers overlying some of the California oil pools. The presence of anaerobic bacteria in recent muds, and doubts of the efficacy of the simple reaction by hydrocarbons at the temperatures prevailing in most sedimentary rocks, have led many workers to attribute the reduction to these bacteria. The point is far from proven, however, and many workers question the ability of the micro-organisms to survive under conditions of deep burial. Gintner (1934) reviewed the problem in some detail.

Comparison with Brine of Other Areas

Brines within a basin tend to be of similar composition regardless of the formation in which they occur, and they tend to resemble each other more closely than they do brines of other basins. Local variations are due chiefly to contamination of meteoric water and to ion-exchange reactions.

Table 5 presents selected analyses from several regions to illustrate the differences between the brines from different parts of the country. Pennsylvania and West Virginia brines resemble each other quite closely. Those of the midcontinent region, as illustrated by the Illinois-Kentucky and Okla-

Table 5. *Composition of brine in percent equivalents*

	Appalachian Basin		Ill.[3] Ky.	Okla.[4]	W. Tex.[5] Permian Basin	Rocky[6] Mtn.	Mich.[7] Salina dolomite
	Pa.[1]	W. Va.[2]					
Calcium (Ca)	11.67	11.08	6.04	7.11	4.01	2.31	45.02
Magnesium (Mg)	3.40	3.90	3.21	3.20	5.20	1.93	2.59
Sodium (Na)	34.72	34.61	40.75	39.69	40.79	45.76	0.00
Potassium (K)	.17	.31					2.39
Ammonium (NH_4)	——	——	.00	——	——	——	present
Strontium (Sr)	.08	.10	——	——	——	——	——
Chloride (Cl)	49.80	49.88	49.60	49.50	42.74	20.65	49.72
Bromide (Br)	.20	.12	——	——	——	——	.19
Bicarbonate (HCO_3)	.00	.00	.07	.04	.96	15.56	.09
Sulfate (SO_4)	.00	.00	.33	.46	6.30	13.79	.00
Mean dissolved solids (Ppm)	92,600	98,800	101,800	102,600	48,900	6,720	——
Maximum dissolved solids in this report (Ppm)	312,000	296,000	170,000	254,000	350,000	38,000	643,000

[1] Based on the 35 samples in this report having less than 140,000 ppm DS— See text, p. 31.

[2] From Hoskins, 1947.

[3] From Meents and others, 1952.

[4] From Case, 1934.

[5] From Berger and Fash, 1934.

[6] From Coffin and DeFord, 1934.

[7] From Case, 1945.

Analyses 2–6 are averages of 10 randomly chosen samples from each of these reports. The only restriction in selection was that each sample contain less than 140,000 ppm for consistency with those from Pennsylvania.

homa analyses, also show mutual consistency, but differ from those in the Appalachian basin, which have a higher sodium to calcium ratio and contain measurable amounts of sulfate and bicarbonate.

Brines from the Permian basin of West Texas show the effects of the closed-basin and evaporite-forming conditions under which the sediments were laid down. Berger and Fash (1934, p. 882) point out that both the composition and concentration of the brine in the rocks at the present time were controlled by the position of the water in the basin at the time it was trapped in the sediments. High total solids and high sodium and sulfate content indicate formation of the brine in deeper water in the basin.

The Rocky Mountain oil-field waters are lower in total concentration and chloride and markedly higher in bicarbonate and sulfate. This is believed due to the flushing of the sands by meteoric water. An unusual feature of these waters is their decrease in concentration with increasing depth (Sage, 1955, p. 79), in contrast with those of other regions. The inversion is probably due to geologic structure which permits greater accessibility of meteoric water to lower formations. The abnormally high sodium content is undoubtedly due to base exchange.

GEOLOGIC FACTORS

Crawford (1951, p. 275) noted the erratic variations in concentration, or dissolved-solids content, of brine obtained from a formation composed of isolated lenses in the Rocky Mountains. Similar variations seem to prevail in brine samples from the Hundred Foot sand in Butler County, Pa., in which the total solids ranged from less than 60,000 ppm to over 135,000 ppm.

The concentration of brine has also been observed to increase downdip within a formation (Price and others, 1937, p. 112). The data for the Berea and Fourth sand in this report appear to bear this out. However, the relationship is not apparent in the other formations—possibly because the wells customarily are not cased below the fresh-water horizons, and the brine in the major aquifer is, therefore, somewhat changed by mixing with saline waters of other formations penetrated by the well.

The increase in concentration of the brine with increase in age of the aquifer has been pointed out by many authors, such as Sage (1955, p. 19), DeSitter (1947, p. 2034), and Hoskins (1947, p. 2), and it also holds true for the data of this report. (See Table 6.)

There is considerable overlap in the concentration of the brine from different formations, and an equilibrium condition has apparently been reached in the older beds such that the dissolved-solids content is about 300,000 ppm in formations older than Middle Devonian. It is also interesting to note that the concentration of brine from the Oriskany for example, is about the same regardless of the depth of burial of the formation.

Table 6. *Concentration of brine from rocks of different ages.*

Age of rocks	Dissolved solids in parts per million	Number of samples
Pennsylvanian (Pottsville)	6,000 to 26,500	2
Mississippian (Pocono)	6,840 to 130,000	12
Devonian (Upper)	55,100 to 177,000	29
Devonian (Middle)	293,000 to 294,000	2
Devonian (Lower)	279,000 to 312,000	4
Silurian (Upper)	190,000	1
Cambrian (Upper)	299,000	1

Brine increases in concentration toward the center of the Pittsburgh-Huntington Basin in West Virginia (Hoskins, 1949, p. 316) and toward the center of the Eastern Interior Basin in Illinois (Meents and others, 1952, p. 8). The data of this report are inadequate to support such a conclusion for areas in western Pennsylvania. Furthermore, the data show no obvious relationship between concentration and position on minor structures (see Figure 2), or between concentration and the presence of oil or gas in the well (see Appendixes 1 and 2).

One of the major causes of variation in the concentration of the brine from place to place is dilution by fresh water. In some areas the dilution may be caused by the natural downslip encroachment of fresh water, such as occurs in all outcrop areas. In other areas, particularly in the northwestern part of the State, meteoric waters may enter the brine aquifer through the glacial sands in a buried valley. In old oil and gas fields, such as those in Pennsylvania, fresh water may be introduced from the upper fresh-water aquifers through leaky casings and by movement around poorly installed plugs. Sites where the first two conditions prevail may be readily delineated by standard geologic mapping techniques. Areas where dilution results from leaky casings and poorly plugged wells, can be defined only through a detailed study of each area.

Deliberate flooding of an oil field for secondary recovery of oil is another way in which dilution of brine occurs. Areas in which this type of dilution occurs are usually easy to define because the flooding is closely controlled and its progress is a matter of record. Information on specific areas may be obtained from Fettke (1950b), Lytle (1950), and the annual progress reports of oil and gas developments in Pennsylvania by Lytle and others.

ORIGIN OF THE BRINE

Most explanations of the origin of natural brine start with the assumption that the brine is an alteration product of connate water (water trapped in the sediments at the time of their deposition). The dissolved-solids concentration of brine ranges from less than that of sea water (see Table 7) in some Late Tertiary brines to nearly 20 times that of sea water in the case of the most concentrated brine yet reported (see Table 5).

The diagenesis of brine results in a decrease in the percentage of magnesium and an increase in the percentage of calcium. The percentage of potassium is reduced, and bicarbonate and sulfate are almost completely depleted, leaving chloride as the chief anion. Strontium, barium, bromide, and the trace elements—iron, manganese, and iodide—are differentially enriched beyond the effects of simple removal of part of the water.

Table 7. *Analysis of sea water*

(After Rankama and Sahama, 1950)

	Parts per million	Percent equivalents
Silica (SiO_2)	0.01 – 7.0	——
Iron (Fe)	.002 – .02	——
Aluminum (Al)	.16 – 1.9	——
Manganese (Mn)	.001 – .01	——
Copper (Cu)	.01 – .09	——
Zinc (Zn)	.005 – .014	
Barium (Ba)	0.05	0.00
Calcium (Ca)	400	1.68
Magnesium (Mg)	1,272	8.81
Sodium (Na)	10,561	38.66
Potassium (K)	380	.82
Lithium (Li)	.1	.00
Strontium (Sr)	13	.03
Chloride (Cl)	18,980	45.09
Bicarbonate (HCO_3)	139.7	.19
Sulfate (SO_4)	2,648.6	4.64
Fluoride (F)	1.4	.01
Nitrate (NO_3)	.001 – 0.7	.00
Phosphate (PO_4)	>.001 – .10	.00
Bromide (Br)	64.6	.07
Iodide (I)	.05	.00
Total solids	34,481.6	100.00

Mills and Wells (1919) noted the clogging of gas sands with sodium chloride crystals in the vicinity of old wells and suggested that the concentration of the brine was due to evaporation of part of the water into migrating gas.

The reversal of the abundance of calcium and magnesium is susceptible to either or both of two explanations: (1) It is due to an ion-exchange reaction which results in the sorption of magnesium and release of calcium to the solution or (2) it is due to the hydrolysis of the magnesium chloride at the high temperatures accompanying deep burial of the sediments and the subsequent attack on calcium carbonate present in the rock. The chemical reactions involved in the second method are as follows:

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl;$$

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

This theory has been reiterated by most writers, including Torrey (1934b) and Price and others (1937).

In 1930, as a result of his work in the Rumanian oil fields, Krejci-Graf (cited in Rankama and Sahama, 1950, p. 358–360) suggested that brine is formed by the same process as petroleum; in fact, the brine is to be considered the main product of the reaction. He noted the biophile character of bromine and iodine and the tendency of potassium to be concentrated in some marine organisms. In addition, he pointed out that plankton may contain as much as 90 percent water. During early stages of the formation of petroleum, the oxygen trapped with the sediments reacted with organic matter, partially decomposing it and releasing water which in turn extracted the inorganic materials. This theory may serve to explain the Rumanian brines which contain 5.67 percent potassium and are Late Tertiary in age, but it is not completely suited to the highly concentrated low-potassium brines of the Paleozoic rocks of the Appalachian basin.

After a study of selected oil fields throughout the world (and especially in the United States), in which the production was from rocks ranging in age from Paleozoic to Tertiary, DeSitter (1947) suggested a two-stage mechanism to account for the constitution of the brines. In the first step of the process, the sediments begin to compact with increasing depth of burial and some of the entrapped water is expelled upward. A part of the calcium and magnesium is removed from solution by precipitation as the carbonate and/or sulfate, and some is removed by adsorption on the clay. The brine at this stage is less concentrated than that of sea water. At some point in the compaction of the sediments these reactions stop, although the circulation of water from bottom to top continues. From this point on, the effective pore spaces in the shales overlying the aquifers are so small that the shales act as semipermeable membranes. As a result, the water molecules are still allowed to pass, but the larger ions of the minerals in solution are strained out and left behind in the aquifers. According to DeSitter some of the pellicular water is eventually squeezed out of the intercalated shales. This water, he states, has been enriched in calcium and magnesium because of the ion-exchange capacity of the clay; therefore, its addition to the brine in the aquifer increases the ratio of calcium and magnesium to sodium.

The decreasing sodium calcium ratios in the very concentrated brines seem to be better explained by ion exchange as discussed on page 32, rather than by the differential enrichment suggested by DeSitter.

Barium, lithium, and potassium normally tend to be concentrated in the hydrolyzate sediments (clays), so that sea water contains far less of them than would be expected from their abundance in rocks. If the adsorbed water on the fine-grained sediments is enriched with these elements, as DeSitter suggests, then a squeezing out of some of this water during the latter stages of compaction could account for the unusually high lithium and potassium concentrations in the very concentrated brines. For the same reason, these brines should contain more barium, than brines of lower concentration, but such is not the case. As most of the barium not adsorbed in the clays is precipitated as the sulfate (barite), the erratic concentrations of barium might be ascribed to the re-solution of this mineral in certain formations.

Strontium, like sodium, reaches the sea in amounts proportional to its natural abundance in rocks. In the sea, it may become a minor constituent in the formation of the aragonite shells of some marine animals, or it may be precipitated as the sulfate. The re-solution of these compounds may, thus, account for the slight enrichment of strontium in the brines.

The relative abundance of iron and manganese may be due to their solubility in reducing solutions such as exist in the presence of organic matter. The biophilic character of bromide and iodide, as pointed out by Krejci-Graf, is probably responsible for their enrichment in the oil-field brines.

SUMMARY

In summary the following points may be stated:

1. Natural brine in Pennsylvania ranges in age from Cambrian to Pennsylvanian and generally increases in concentration with increasing age of the producing zone. Local and marked exceptions to this rule may occur owing to dilution by meteoric water.
2. Information on the occurrence of brine in Pennsylvania is available only within the limits of production of petroleum and natural gas and, hence, its occurrence is known in greatest detail in the "shallow sands" (Upper Devonian or younger) and in the Oriskany formation. The most productive brine-producing zones among these sands are the Oriskany formation and the Hundred Foot, Murrysville, Berea, Big Injun, Mountain, and Salt sands. The Upper Devonian formations are devoid locally of "free" water, especially where the formations consist of red beds.
3. Data collected during this investigation do not reveal any effect of local or regional structure on the composition or concentration of the brine, and reveal only a little evidence of the effects of rock type, although these effects are well substantiated in the literature of other areas.
4. The hydrology of brine zones differs from that of fresh-water aquifers in two important respects: First, the supply of brine is limited, like that of the oil and gas, and is not renewable as is that of fresh water; second, the presence of gas in the aquifer invalidates the standard quantitative techniques used by hydrologists for evaluating aquifers; because of this, little information is available concerning the hydraulic characteristics of the brine zones in Pennsylvania.
5. Well-defined relations with a high degree of correlation and known

standard error of estimate are shown to exist between dissolved-solids and density and between dissolved-solids and the following ions: chloride, sodium, calcium, magnesium, bromide, and strontium. Some of these relations are not linear at higher concentrations, possibly because of ion-exchange reactions. The exact point at which this happens is uncertain because of the scarcity of data for concentrations above 140,000 ppm.

6. Poorer correlation was obtained between dissolved-solids and potassium, because of a few (3) samples whose high concentration is apparently due to local lithologic factors.

7. A relation exists between dissolved-solids and specific conductance, for which the square root of the dissolved-solids serves as a first approximation.

8. Barium and the trace constituents, silica, iron, aluminum, manganese, copper, zinc, lithium, fluoride, iodide, bicarbonate, and sulfate, which are present usually in amounts less than a few tens of ppm, are essentially independent of dissolved-solids.

9. DeSitter's (1947) explanation of the origin of the brines, which postulates a two-stage mechanism of concentration of sea water, is accepted here with slight modification. The first stage is the removal of some of the calcium and magnesium by precipitation as carbonates and/or sulfates and possibly by ion exchange, and a reduction of concentration to less than that of sea water. The second stage is the concentration of the brine by removal of part of the water, essentially by filter pressing through the compacted shales which act as semipermeable membranes. The higher calcium-sodium ratio is accounted for by the ion-exchange reaction which takes place in highly concentrated sodium chloride solutions.

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Appendix 1.—Records of wells

County	Well number	Field	Owner	Date completed	Altitude above sea level (feet)	Diameter of casing (inches)	Total depth (feet)	Depth to bottom of casing (feet)	Aquifer		Aquifer depth (feet)		Use	Static water level below land surface (feet)
									Name	Composition	From	To		
Lawrence	101	Bessemer	Mrs. D. Moritz	1910	1,150	6-1/4	700	400	Berea formation	Sandstone	650	690	Oil	
Do.	102	do.	do.	1911	1,130	6-1/4	697	400	do.	do.	648	690	Oil	
Butler	201	Rosenberry	Ralph McGinnis		1,480	4-1/4		762	Hundred Foot sand	do.	1,280		Oil	
Do.	202	do.	do.		1,460	6	1,200	500	do.	do.	1,280		Oil	
Do.	203	Callery-Watters	E. P. Gifford	1948	1,194	6-1/4	1,500	1,392	do.	do.	1,420		Oil	
Do.	204	do.	Verne Pervis		1,180	5		1,400	do.	do.	1,400		Oil	
Do.	205	Crider-Duncan	R. S. Steeb		1,008				do.	do.	1,350		Oil	
Do.	206	do.	do.		1,012				do.	do.			Oil	
Do.	207	Thorn Run	Ritzert Bros.	1941	1,227	6-1/4	1,288	570	do.	do.	1,236	1,288	Oil	
Do.	208	do.	do.		1,169	6-1/4		517	do.	do.	1,179		Oil	
Do.	209	East Butler	E. Rodgers		1,130	6-1/4	1,230	472	do.	do.	1,160	1,220	Oil	
Do.	210	Oneida	W. J. Derr		1,280				do.	do.	1,315	1,328	Oil	
Do.	211	do.	H. B. Kiser		1,103	6-1/4	1,606	454	do.	do.	1,081	1,195	Oil	
Do.	212	Jefferson Center-Hunter	F. A. Cramer	1909	1,280	6-1/4	1,387	516	do.	do.	1,338		Oil	
Do.	213	do.	Eugene Geibel	1906	1,156	6-1/4	1,366	570	do.	do.	1,322		Oil	
Do.	219	Chicora	do.	1905	1,300	5-5/8	1,600	500	Mountain sand	do.	675		Oil	
Do.	220	Muddy Creek	W. M. Ruby Estate	1939	1,470	4-7/8	1,000	600	Berea formation	do.	956	980	Oil	
Do.	221	do.	do.	1939	1,420	4-7/8	1,000	600	do.	do.	960	984	Oil	
Do.	222	Chicora	George Hildebrand	1900	1,180	5-5/8	1,600	450	Mountain sand	do.	650	700	Oil	

Appendix 1.—Records of wells (continued)

County	Well number	Field	Owner	Date completed	Altitude above sea level (feet)	Diameter of casing (inches)	Total depth (feet)	Depth to bottom of casing (feet)	Aquifer		Aquifer depth (feet)		Use	Static water level below land surface (feet)
									Name	Composition	From	To		
Butler	223	Bakerstown	R. W. Freese	1898	1,210	4-7/8	1,900	1,620	Third sand	Sandstone	1,840		Oil	
Do.	224	do.	do.	1904	1,225	4-7/8	1,850	1,600	do.	do.	1,815		Oil	
Do.	225	Crider Duncan	R. J. Steeb	1958	1,060	6-5/8	1,925	700	Murrysville sand	do.	1,225	1,315	Oil	
Do.	226	Shira Streak	Neil King		1,390	4-7/8	1,350	500	Hundred Foot sand	do.	1,104	1,124	Oil	
Do.	227	do.	do.		1,485	6-1/4	1,420	570	Shira sand	do.	1,398		Oil	
Do.	228	Hooker	Dale Albaugh		1,300		1,550		Fourth sand	do.	1,515	1,550	Oil	
Beaver	501	Crow's Run	Harvey Kline and others	1958	1,160	6-1/4		505	Murrysville sand	do.	1,260			800
Do.	502	Hookstown	George Dawson	1889	1,080	5-5/8	1,175	450	Berea formation	do.	1,150			
Do.	503	do.	do.	1938	1,080	6-1/4	1,171	446	do.	do.	1,148		Oil	
Allegheny	601		Waverly Oil Works	1893	1,100	5-3/16		2,197	Fifth sand	do.	2,248	2,275		
Do.	602		do.	1894	1,179	4-7/8		1,424	Hundred Foot sand	do.	2,227	2,242		
Do.	603		Equitable Gas Company	1912	1,000	6-5/8	2,089	2,078	Gordon sand	do.	2,038	2,089	Oil	
Washington	701		Waverly Oil Works	1893	1,134	6-1/4	2,341	1,313	do.	do.	2,312	2,335	Oil	
Do.	702		do.	1894	1,060	4-7/8		1,325	Fourth sand & Gordon sand	do.	2,280	2,295	Oil	
Do.	703		Manufactures Light & Heat	1910	1,280	6-5/8	1,538	1,453	Salt sand	do.	1,453	1,508	Oil	

Do.	704		do.	1924	1,120	8	1,349	1,140	do.	do.	1,285	1,349	Oil	
Do.	705		Washington Oil Company	1890	1,040		2,368	1,437	Gordon sand	do.	2,343	2,355	Oil	
Do.	706		do.	1890	1,045		2,544	1,515	Fifth sand	do.	2,515	2,538	Oil	
Do.	707		do.	1890	1,070		2,522	1,447	Gordon sand	do.	2,492	2,504	Oil	
Do.	708		do.	1896	1,300		2,867	1,750	Fourth sand	do.	2,826	2,840		
Do.	709		do.	1895	1,130		2,410	1,570	Fifty Foot sand	do.	2,359	2,405		
Do.	710		do.	1936	1,300		3,050	2,978	Fifth sand	do.	3,018	3,050		
Westmoreland	801		Peoples Natural Gas Company	1912	1,270	5-3/16	1,403	752	Murrysville sand	do.	1,344	1,403	Gas	
Do.	802		do.	1917	1,216	6-5/8	1,318	1,174	do.	do.	1,246	1,318	Gas	
Westmoreland	803	St. Boniface Chapel Gas Pool	Peoples Natural	1957	1,840		7,565	7,475	Onondaga limestone	Chert	7,475	7,565		
Do.	804	do.	do.	1957	1,772		7,435	7,229	Onondaga limestone and/or Oriskany sandstone	Chert or Sandstone	7,226 7,377	7,377 7,435		
Clearfield	1101	Rockton	Manufactures Light & Heat	1958	1,625	7	7,396	7,249	Oriskany sandstone	Sandstone	7,370			Flowing
Do.	1102	do.	New York State Natural Gas	1958	1,495	5-1/2	7,292	7,211	Oriskany sandstone	do.	7,267	7,291		800
Do.	1103	do.	F. C. Deemer	1958	1,648	7	7,600	7,490	do.	do.	7,528	7,550		900
Erie	1201	Roberts Pool	Britton and others	1958	883	7	2,644	2,398	Salina formation	Anhydrite and dolomite	2,320			
Do.	1202	Goodwill Curley	V. R. Stephens	1956	1,240	7	6,015	3,506	Gatesburg formation	Dolomite	5,970	5,987		4,230
Do.	1203		Prath Farm	1955	893		2,005	1,743	Oriskany sandstone	Sandstone	1,997			5

Appendix 2.—Chemical analyses of brines

(Results in parts per million except specific conductance, pH, and density)

Well No.	Aquifer	Silica (SiO_2)	Aluminum (Al)	Iron (Fe)	Manganese (Mn)	Copper (Cu)	Zinc (Zn)	Calcium (Ca)	Magnesium (Mg)	Strontium (Sr)	Sodium (Na)	Potassium (K)	Lithium (Li)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Bromide (Br)	Iodide (I)	Nitrate (NO_3)	Phosphate (PO_4)	Dissolved solids		Specific conductance (micromhos at 25° C.)	pH	Density (gms/ml at 20° C.)
																						Calculated	Residue on evaporation at 180° C.			
703	Salt sand	3.7	0.0	0.13	0.03	0.05	0.15	32	8.9	5.9	2,030	14	0.0	583	0.0	2,810	1.6	159	4.5	28	0.0	5,390	6,000	9,220	7.8	1.001
704	do.	5.4	.0	39	1.2	.42	.00	2,050	290	18	7,080	68	1.0	206	.0	15,000	.7	84	20	4.9	.0	24,800	26,500	36,300	6.6	1.014
219	Mountain sand	28	.0	63	1.5	.96	.00	8,460	1,320	207	32,200	163	9.0	0	.0	69,300	.4	477	25	49	.2	112,000	127,000	140,000	4.30	1.082
222	do.	12	.0	64	1.5	.91	.00	7,810	1,210	196	28,900	138	7.5	0	.0	62,500	.0	432	20	58	.1	101,000	115,000	132,000	3.83	1.074
101	Berea formation	9.2	.0	15	.50	.00	.00	4,500	1,120	279	17,600	66	7.0	103	.0	39,300	1.4	188	7.6	57	.0	63,200	71,000	98,700	7.7	1.049
102	do.	12	.0	33	1.0	.00	.00	3,300	865	79	14,200	16	4.0	125	.0	30,000	.5	182	5.5	48	.0	48,800	54,000	78,000	7.7	1.033
220	do.	30	.0	61	2.7	1.4	.00	7,850	1,470	94	28,300	130	6.0	0	.0	62,100	.0	492	11	44	.2	101,000	112,000	133,000	4.5	1.074
221	do.	16	.0	45	1.7	1.0	.00	5,760	1,080	64	20,600	99	4.0	28	.0	45,600	.0	368	12	34	.2	73,700	85,400	102,000	5.6	1.053
502	do.	19	.0	120	24	2.0	.00	8,790	1,740	57	28,500	122	4.0	98	.0	64,900	.9	577	14	61	.1	105,000	121,000	140,000	5.4	1.078
503	do.	17	.0	67	38	1.4	.00	8,000	1,850	62	26,600	123	3.0	244	.0	60,600	.2	339	12	58	.1	97,900	116,000	135,000	6.2	1.073
225	Murrysville sandstone	6.5	.0	35	.79	.25	.56	1,380	295	14	6,760	63	4.2	184	.0	13,800	.3	105	2.9	12	.0	22,600	25,000	46,300	6.6	1.014
501	do.	9.9	.1	112	1.9	.00	.00	1,810	450	33	12,100	66	3.0	0	.0	23,500	.0	252	3.9	34	.0	38,400	43,000	68,200	4.00	1.028
801	do.	8.4	.0	2.0	.07	.06	.32	417	31	2.1	1,980	12	2.0	227	.0	3,790	.6	32	.8	.0	.0	6,390	6,840	11,400	7.4	1.001
802	do.	5.8	.0	89	.73	.07	.81	9,670	1,410	210	34,100	179	36	0	.0	74,300	.1	625	20	34	.0	121,000	130,000	153,000	4.33	1.089
201	Hundred Foot sand	16	.0	31	7.8	.00	3.5	5,310	1,070	64	18,100	67	3.8	204	.0	40,500	.0	255	11	12	.0	65,600	70,600	89,800	6.8	1.048
202	do.	8.9	.0	4.6	11	.20	8.3	6,610	1,300	84	22,200	85	4.9	263	.0	50,100	.0	197	14	22	.2	80,800	86,800	116,000	6.7	1.059
203	do.	14	.0	40	1.8	.00	4.6	6,750	1,290	92	24,100	131	6.8	0	.0	53,600	.0	427	13	42	1.7	86,600	91,900	119,000	4.40	1.065
204	do.	14	.0	40	2.4	.00	2.0	7,240	1,360	96	25,400	128	7.1	1.1	.0	56,100	.0	440	13	42	5.3	90,900	96,300	120,000	4.6	1.068
205	do.	12	1.1	55	4.4	.42	.00	9,900	1,760	110	31,000	177	12	0	.0	71,000	2.6	496	17	63	.0	115,000	124,000	140,000	4.5	1.086
206	do.	10	.9	58	4.1	.30	.59	9,690	1,740	114	29,900	170	12	7.0	.0	68,200	.4	114	18	51	.0	110,000	121,000	146,000	5.0	1.085
207	do.	8.5	1.1	46	.88	.28	.00	8,120	1,440	101	27,900	145	7.0	18	.0	61,800	.9	581	17	64	.0	100,000	113,000	139,000	5.2	1.074
208	Hundred Foot sand	9.0	0.0	38	.91	.00	.00	9,140	1,460	108	27,000	62	7.0	64	.0	62,300	0.0	217	6.6	51	.0	100,000	103,000	130,000	6.6	1.071

209	do.	8.9	1,3	52	1.4	.48	.00	9,410	1,660	113	32,800	154	9.0	2	.0	72,600	.9	635	13	59	.0	117,000	130,000	143,000	4.6	1.088
210	do.	7.8	1.3	50	4.5	.27	.00	10,400	1,720	126	33,500	168	7.5	6	.0	75,700	1.1	650	23	61	.0	122,000	135,000	150,000	4.7	1.092
211	do.	8.7	.4	55	3.7	.11	.00	9,210	1,540	112	29,900	155	6.0	0	.0	66,800	1.3	619	21	60	.0	108,000	120,000	128,000	4 5	1.081
212	do.	8.8	.1	61	1.2	.00	.00	10,200	1,090	122	33,400	98	7.5	136	.0	73,200	1.8	99	16	118	0	118,000	131,000	140,000	7.6	1.093
213	do.	13	.0	26	1.0	.00	.00	4,200	1,190	52	14,800	80	2.5	0	.0	33,300	1.0	6.7	7.6	24	.0	53,700	57,700	77,100	4.5	1.039
226	do.	—		—	-	—	--	10,600	1,980	—	36,500	456				79,900		686	21			-	136,000	155,000	4.7	1.097
602	do.	11	.5	76	2.0	1.1	.00	9,250	1,550	110	30,500	177	7.9	2	.0	68,400	1.8	586	22	65	.0	111,000	124,000	139,000	4.6	1.082
709	do.	—	—	—	—	—	—	--		—	—	-	-			70,600		560	18				118,000	141,000	4 7	1.083
227	Shira sand				—		—	-		—	—	—	—	—	—	52,500		444	13	—			92,700	114,000	5.4	1.062
603	Gordon sand							12,700	1,900	—	36,300	653				84,900	–	769	26			—	166,000	156,000	4.00	1.102
701	do.	9.0	1.7	57	24	2.8	.00	15,900	2,220	70	40,700	203	8.0	0	.0	97,400	2.0	966	36	78	.0	158,000	177,000	180,000	4.40	1.122
705	do.	—	—	—	—	—	—	3,460	722	–	15,900	481	–	—	—	34,500		242	5.9				59,300	77,600	4 90	1.039
707	do.							6,620	1,290	—	25,200	451		-		55,400		443	12				95,600	117,000	4.30	1.064
223	Third sand	3.1	.0	67	.73	.43	.06	9,940	1,740	122	28,500	157	7.4	4	.0	67,100	.2	566	17	44	.0	108,000	119,000	148,000	5.0	1.080
224	do.	5.7	.0	81	.19	.51	3.7	3,400	623	37	11,900	68	5.5	30	.0	26,500	.4	217	7.8	16	.0	42,900	55,100	61,000	5.8	1.029
228	Fourth sand						-			—	—	—	--	.		71,800		587	17				114,000	144,000	3.85	1.088
702	do.	11	.9	34	13	.70	.00	11,000	1,280	79	29,400	148	6.5	9	.0	68,300	2.6	665	28	66	.0	111,000	126,000	139,000	5.0	1.082
708	do				-			-		—	--		-			80,000	—	688	19				141,000	155,000	4.10	1.096
601	Fifth sand	10	1.0	17	8.5	,85	.00	8,590	1,320	66	26,200	172	6.5	33	.0	59,500	1.3	551	20	63	0	96,500	108,000	127,000	5.9	1.071
706	do.		-		--	—	--	-	—	--	—	—		-		61,100		481	11				106,000	127,000	4.8	1.071
710	do.			-						-	—					90,300		817	27	—		—	155,000	169,000	4.40	1.111
803	Onondaga limestone	25	0.2	200	1.8	0.74	13	32,200	2,120	321	65,700	2,490	217	0	.0	166,000	3.3	1,080	28		.0	272,000	294,000	218,000		1.223
804	do.	23	.0	290	.72	1.5	10	31,600	2,350	304	66,100	2,190	219	0	.0	166,000	21	1,060	13		.0	272,000	293,000	220,000		1.222
1101	Oriskany sandstone							35,900	3,510		57,100	3,260		—		169,000		1,440	8 6	-			312,000	210,000	2.35	1.226
1102	do.				—	—	—	34,700	1,250	—	55,000	2,780		—	—	154,000		1,260	5.6				279,000	209,000	2.65	1.200
1103	do.					--	—	38,400	3,700	—	56,200	3,260		-		170,000	-	1,400	23	—		—	311,000	210,000	3.20	1.228
1203	do.		30	3.9	1.70	.15	2.0	37,300	8,280	- -	42,800	3,970	187	176	528	161,000	2.3	1,770	32		-	256,000	294,000	215,000	6.5	1.216
1201	Salina formation		-			-		22,900	3,520	—	28,600	3,180		—		96,200		970	11		-		190,000	166,000	6.1	1.118
1202	Gatesburg formation	44	0.0	3.7	4.8	-	.00	31,700	4,180		61,000	3,640	154	190	581	162,000	2.5	1,780	19			265,000	299,000	222,000	6.9	1.219

Appendix 3.—Spectrographic analyses

(Parts per million)

*: Present, but not determined quantitatively; estimated to be from 0.1-1.0 percent of total solids.
N. D.: Not detected.
Trace: Less than 0.1 percent of total solids.
---: Not determined.

Formation	Well number	Iron (Fe)	Manganese (Mn)	Strontium (Sr)	Barium (Ba)	Lithium (Li)	Rubidium (Rb)	Cesium (Cs)	Boron (B)
Salt sand	703	0.19	0.04	4.7	1.9	N.D.	---	---	0.8
Do.	704	50	.67	18	23	N.D.	---	---	N.D.
Mountain sand	219	78	2.7	179	403	N.D.	---	---	N.D.
Do.	222	81	1.9	192	656	N.D.	---	---	N.D.
Berea sandstone	101	12	.50	284	1,080	Trace	---	---	N.D.
Do.	102	42	.68	59	478	N.D.	---	---	N.D.
Do.	220	86	2.9	97	59	N.D.	---	---	N.D.
Do.	221	56	3.8	54	38	N.D.	---	---	N.D.
Do.	502	250	23	54	10	N.D.	---	---	N.D.
Do.	503	70	31	63	6.0	N.D.	---	---	N.D.
Murrysville sand	225	---	---	---	97	4.1	<0.2	0.	---
Do.	501	96	6.9	*	165	N.D.	---	---	N.D.
Do.	801	---	---	---	36	1.3	0.	0.	---
Do.	802	---	---	---	218	24	0.	0.	---
Hundred Foot sand	201	34	12.5	*	10.5	N.D.	---	---	N.D.
Do.	202	3.2	11.3	*	14.5	N.D.	---	---	N.D.
Do.	203	42	2.1	*	407	Trace	---	---	N.D.
Do.	204	45	2.3	*	564	Trace	---	---	N.D.
Do.	205	63	5.9	*	414	Trace	---	---	N.D.
Do.	206	66	5.3	*	440	Trace	---	---	N.D.
Do.	207	43	.83	*	120	N.D.	---	---	N.D.
Do.	208	41	.83	*	97	N.D.	---	---	N.D.
Do.	209	55	1.3	*	71	N.D.	---	---	N.D.

Hundred Foot sand	210	46	5.1	*	9.5	N.D.	---	---	N.D.
Do.	211	53	3.8	*	28	N.D.	---	---	N.D.
Do.	212	72	3.9	*	53	N.D.	---	---	N.D.
Do.	213	26	.70	*	34	N.D.	---	---	N.D.
Do.	602	120	3.1	101	97	N.D.	---	---	N.D.
Gordon sand	701	63	17	66	5.1	N.D.	---	---	N.D.
Third sand	223	---	---	---	43	6.5	0	0	---
Do.	224	---	---	---	86	4.3	0	0	---
Fourth sand	702	41	11	74	10	N.D.	---	---	N.D.
Fifth sand	601	15	8.4	64	7.1	N.D.	---	---	N.D.
Onondaga limestone	803	---	---	---	920	63	<3	0	---
Do.	804	---	---	---	1,140	93	<3	0	---